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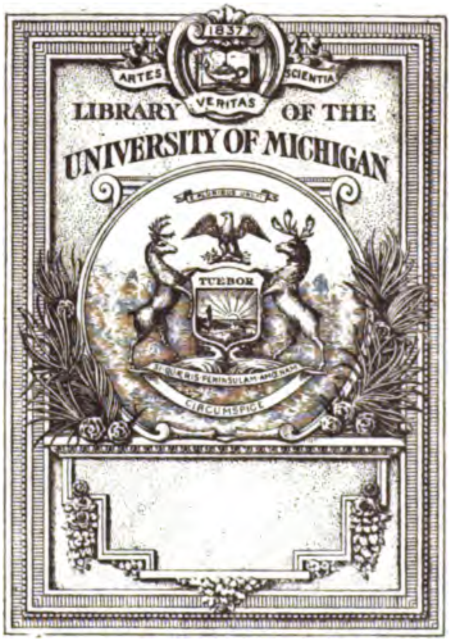
WHITE'S
QUALITATIVE CHEMISTRY



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EXERCISES

IN

QUALITATIVE CHEMISTRY

CHIEFLY INORGANIC

BY

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PREFACE.

It is well known to all who give instruction in the details of analytical work that students, when provided with a text-book, are prone to rely too implicitly upon the descriptive matter there furnished, and consequently neglect to pay sufficient attention to their own observations, or to draw conclusions from them.

It was my purpose, in preparing this little manual, to provide the student with a set of laboratory directions which could be used in conjunction with text-books, or otherwise, and which, if conscientiously followed, would enable him to develop for himself, by purely inductive methods, a fairly complete conception of analytical processes. It is not, however, the intention that the manual should in any sense supplant the teacher; on the contrary, it is my firm conviction that satisfactory results in analytical work can be obtained only through the careful oversight, the suggestive questioning, and the frequent discussion, with the class, of the theories and practices involved in the work, such as a good instructor only can give. In this way the student's mind is kept on the alert, he is encouraged to think and reason for himself, and thus acquires that self-reliance so essential to the well-trained chemist. He should, furthermore, be encouraged to broaden his knowledge of the general princi-

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ples of chemistry by frequent reference to the literature of the subject.

In order that this plan might be logically carried out, and that neither teacher nor student should be too much hampered by set rules of procedure, I have purposely omitted such explanatory matter as is usually to be found in text-books, presenting only so much as may be necessary to furnish a basis for the study of each group or class of elements. It is expected that the student shall be able, by a comparison of the reactions studied, to draw conclusions enabling him to perform the operations necessary for the separation and identification of the various elements here described. Recognizing a natural tendency on the part of every student to formulate these facts, I have encouraged him to do so, and, it generally happening that several theoretically possible methods of attaining the end sought are conceivable, the teacher should make it his object to discuss these with the student, pointing out the reasons for favoring one rather than another of them.

In the arrangement of the subject-matter, the plan followed has been in general that adopted by such standard works as Fresenius, Menschutkin, Newth, and others, with such variations as have seemed to me desirable for the sake of clearness. Only the commoner elements have been included. These have been arranged under the general headings "Base-Forming" and "Acid-Forming", those falling under each division being separately considered.

The metallic elements are classified, as usual, into "groups", the classification being based primarily upon the solubilities and conditions of formation of the sulphides. The order in which the groups are numbered is the order in which they are studied, rather than that in which they are used in analytical practice. There is at present so much confusion with regard to this that it is to be hoped some uniform system of group numbering, if not of group arrangement, may soon be agreed upon.

In the case of each metal the object has been to provide a sufficiently extensive set of reactions for study, so that the student might acquire a sufficiently broad knowledge of the various elements to enable him to institute comparisons; these in turn leading him to the desired reactions necessary for purposes of grouping, of separation, or of identification. To this end four general reagents have commonly been employed, viz., the alkaline hydroxides (including ammonia), the alkaline carbonates, hydrogen sulphide and the alkaline sulphides. In addition, certain distinctive reactions have been introduced in the case of each element. In conformity with the general purpose of the book—that of requiring the student to obtain information for himself—no attempt has been made to differentiate, by use of various-sized type, between the various reactions, though obviously they are not of equal value from a purely analytical point of view.

The method of classification, as well as the plan of study, employed in the case of the "acid-forming" elements differs very materially from that pursued in dealing with the metallic elements. The acids do not lend themselves readily to arrangement into groups;

such groups, moreover, when formed, having but little analytical value. The general reactions, therefore, are not given so much prominence as those special reactions which are used for purposes of identification of the acids. A system of grouping, based upon the general behavior of the acids upon silver and barium salts, is, however, for convenience, placed at the end of the book.

The appendix includes systematic methods of procedure in making a preliminary study of unknown substances, as well as the mode of procedure in effecting the solution of solids. A table of solubilities of the more common compounds is also included.

No pains have been spared to make the subject-matter reliable. Naturally the greater part of it has been taken from the standard text-books upon the subject, nearly all of which have been consulted, but much has also been obtained from the current periodicals, references being given in each case, while some is new or represents modifications of older methods. With few exceptions, all the reactions given have been tested by several years' use in my own laboratory.

I am glad to take this occasion to express my gratitude to my friends; to Professor Samuel Avery, of the University of Idaho, for valuable suggestions regarding the compilation of the book; to Mr. R. S. Hiltner, who was so kind as to review the proof; and to Miss A. M. Quaintance, who kindly assisted in the preparation of the subject-matter.

JOHN WHITE.

LINCOLN, NEBRASKA,
March 1901.

INTRODUCTION.

In order to attain success in chemical analysis the student must not only be familiar with ordinary chemical phenomena, but he must be able to evaluate these; to select from the large number of reactions exhibited by an element in its various combinations those which are of chiefest value in enabling him to establish with absolute certainty the presence of that particular element.

To accomplish this he must make a careful study of the properties of the elements under varying conditions, repeated often enough to make them familiar, compare these, and, as a result of the experience thus gained, select for practical use those which are preeminently characteristic of each element. These are comparatively few in number, and it is frequently advisable to use all or several of them for the complete identification of an element, hence they should be thoroughly understood.

In carrying out the various operations in connection with such study it is necessary that the student should observe the greatest care; often an imperfect fusion, a faulty precipitation, or insufficient digestion brings about results leading to erroneous conclusions. Too hasty a deduction from the facts observed should be avoided; all the results obtainable should be noted, and only in the event that they point to the same conclusion is that conclusion justified—not every *green* solution contains chromium, nor every *yellow* precipitate, cadmium. Further, it is evident that if he desires to be sure of his facts, the student must always be in control of the conditions under which those facts are obtained. This is possible only where strict heed is paid to the utmost cleanliness of apparatus and to the complete and accurate carrying out of every operation undertaken. He must, moreover, carry this out according to a definite plan—not experiment at random—knowing beforehand what results are to be expected from each operation, but never with so prejudiced a view as not to see results *exactly* as they exhibit themselves; in other words, be strictly honest in his dealings with himself, since only in this way can accuracy be attained.

Of the various operations most used in chemical investigation, those which have to do with solution and precipitation are of greatest importance. Modern science has demonstrated that a solution is something more than a mechanical mixture of solvent and dissolved substance, that in such a case we are not dealing with the substance in solution *per se*, but with a condition of matter known as the *ion*, and that it is this which is reactive, bringing about chemical changes. Especially is this true of water solutions, which are those with which we have most frequently to do in chemical analysis.

Under these conditions we do not apply a test for iron, or chlorine, or lead, or sulphuric acid, but instead for the *ions* into which compounds of these may split up on going into solution; e.g., we can readily detect the iron and sulphuric acid in ferrous sulphate by applying tests for the *ions* of Fe and SO_4, while we cannot in a similar manner detect the iron in potassium ferrocyanide, because here we have to do, not with the *ion* of iron, but with *ions* of K and $Fe(CN)_6$.

The whole science of chemical analysis is in reality based upon such considerations, and it is evident that the analytical chemist who wishes to understand the science of his subject must familiarize himself with the nature and theory of solution. The limitations of this work do not permit a discussion of these theories here, and the author must content himself with the recommendation to the student that he consult some of the treatises dealing more especially with the subject.[1]

For particulars concerning other operations used in analysis, such as fusion, evaporation, precipitation, the filtering, washing and drying of precipitates, etc., the student is referred to one of the larger text-books (Fresenius, Menschutkin, Newth, and others) where these matters have been fully discussed.

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[1] There are many of these, dealing with different phases of the subject; those which the student will find especially helpful are: Ostwald's "Foundations of Analytical Chemistry"; Walker's "Introduction to Physical Chemistry"; Van Deventer's "Physical Chemistry for Beginners"; Jones' "The Modern Theory of Solution"; Whetham's "Solution and Electrolysis," etc., etc.

PART I.

THE METALLIC OR BASE-FORMING ELEMENTS.

THE METALLIC OR BASE-FORMING ELEMENTS.

In making a study of the chemical elements from an analytical standpoint only those properties of the individual element or of its compounds need be considered which will enable us to separate that element from others or which will serve for its complete identification. For this purpose attention must be paid especially to differences in behavior toward a given reagent, to differences in solubility under similar conditions, or to variations in color either of salts or of volatile compounds when heated, as in making the flame test; or, finally, to differences in behavior under the influence of heat, resulting in decomposition, volatilization, etc.

Of these, that set of properties most frequently made use of is the one involving differences in solubility. It is evident that for purposes of systematic arrangement the selection of any particular class of compounds whose solubilities are to be used is largely arbitrary, but experience has shown that the one class that admits of use as a basis for the simplest classification is the sulphides. With few exceptions, the metals unite with sulphur forming stable salts, which are for the most part insoluble in water, but which present considerable variations of behavior when treated with other solvents.

Based upon a consideration of the properties of the sulphides, we may arrange the base-forming elements into two general divisions, viz.,

DIVISION I.—METALS WHOSE SULPHIDES ARE SOLUBLE IN DILUTE ACIDS.

DIVISION II.—METALS WHOSE SULPHIDES ARE INSOLUBLE IN DILUTE ACIDS.

Each of these may be further subdivided into groups by taking into consideration their behavior toward some other common reagent. The results of this grouping will appear in the following pages.

DIVISION I.

METALS WHOSE SULPHIDES ARE SOLUBLE IN DILUTE ACIDS.

GROUP I.—THE METALS WHOSE SULPHIDES AND CARBONATES ARE SOLUBLE IN WATER.

Under this heading are included the metals of the alkalies: Potassium, Sodium, the hypothetical metal, Ammonium, and Lithium. There being no general group reagent, it becomes necessary in the course of an analysis to apply separate tests for these *after* the removal of the bases of the other groups (ammonium, however, is always to be tested for in a portion of the original substance).

The metals constituting this group exhibit very similar properties. With few exceptions their compounds are readily soluble, are stable in solution and also under the action of heat (ammonium compounds excepted). Lithium, however, differs in some respects quite markedly from potassium and sodium, forming a difficultly soluble carbonate and phosphate, wherein it more closely resembles the elements of the succeeding group, calcium, barium, etc.; indeed it serves in a sense as the connecting link between the two groups.

The fact that so few compounds of these metals are insoluble limits the number of possible reactions which may be used to characterize them, and gives an added prominence to the flame colorations and spectroscopic tests, which are most frequently relied upon for their detection.

POTASSIUM.

Reactions of the Solid.—Heat small portions of several potassium salts (e. g., the chloride, nitrate, sulphate, carbonate, etc.) in ignition-tubes, note what takes place in each case, and explain any differences observed; what conclusion may be deduced as to the stability of potassium compounds when heated? Hold fragments of each of the above salts on a clean platinum wire in the non-luminous flame of the Bunsen burner (‡).[1] Examine the flame through a piece of cobalt glass (‡). Test the solubilities of the salts of potassium, also their reaction towards litmus paper and tabulate.

Reactions in Solution.—*Use a moderately concentrated solution of potassium chloride.*

To a small portion in a test-tube add tartaric acid in excess (‡); divide into two portions, allow one to stand and shake the other; note any observed difference in the readiness with which precipitation ensues. Repeat, using dilute solutions (‡); add a little sodium acetate (‡); determine the delicacy of the reaction. Try the solubility of the precipitate in hot and cold water, in sodium hydrate, sodium carbonate, and in acids (‡).

From the above determine the best conditions for carrying out this test for potassium (‡).

To a few drops of the neutral chloride solution on a watch-glass add several drops of platinum chloride and allow to stand (‡); try the solubility in hot and cold water, in hydrochloric acid, and in alcohol (‡). How could the test be best carried out in the case of potassium salts other than the chloride (e.g., the sulphate)?

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[1] The sign (‡) is intended, throughout, to call the student's attention to the reaction to be noted.

Several other substances yield more or less characteristic reactions for potassium—perchloric acid, hydrofluorsilicic acid, and sodium-cobalto nitrite each give precipitates.

Make the spectroscopic tests for potassium, using the salt of a volatile acid (‡).

SODIUM.

Reactions of the Solid.—Try the effect of heat upon the various sodium compounds, as in the case of potassium (‡). Compare the stability and solubility of sodium salts with the corresponding salts of potassium (‡); also the reaction on litmus (‡).

Note the flame coloration (‡); when seen through cobalt glass (‡) (sometimes, if the cobalt glass is thin, two pieces give better results).

Reactions in Solution.—*Use the chloride.*

Try the effect of tartaric acid in excess upon both dilute and concentrated solutions (‡); compare with potassium.

Add to a few drops of the solution on a watch-glass several drops of a ten per cent solution of platinum chloride (‡); evaporate cautiously, but not quite to dryness, and allow to cool (‡). Determine the solubility of this salt in water and in alcohol, and compare with the corresponding salt of potassium (‡). Would it be possible to use this difference as a means of separating sodium from potassium? Give details.

To a small quantity of the sodium salt add a clear solution of potassium pyroantimoniate (‡). Try the solubility in hot and cold water, in alkalies and in acids (‡); try similar reactions with the pyroantimoniate alone (‡). Note all conditions of reaction in this test—it gives the only insoluble simple salt of sodium.

Make the spectroscopic tests for sodium, using salts of volatile acids (‡).

AMMONIUM.

Reactions of the Solid.—Heat in a test-tube or small crucible small portions of each of the following ammonium salts: Ammonium chloride, nitrate, sulphate, carbonate, and oxalate; note what happens in each case, together with any differences observed (‡). Compare with potassium and sodium salts (‡).

Treat any of the above salts on a watch-glass with a solution of sodium hydrate; odor (‡). Make a moderately dilute solution of the salt and treat in the same way in the cold, then on warming (‡); hold above the vessel moistened red litmus paper, paper moistened with a solution of mercurous nitrate, and turmeric paper respectively (‡). Moisten stirring-rods with hydrochloric, nitric or acetic acids, and hold these above the vessel (‡) (why not use sulphuric acid?). Determine the delicacy of these tests by diluting the ammonium salt solution more and more (‡)—for very delicate tests moisten a piece of red litmus paper and attach it to the lower side of a watch-glass used to cover the vessel in which the reaction is carried out.

Reactions in Solution.— *Use the chloride.*

Treat concentrated solutions of ammonium chloride and carbonate respectively with tartaric acid in excess (‡); compare with potassium as to delicacy of reaction, solubility of the precipitate, etc. (‡). The precipitate can easily be distinguished from that of the potassium compound by complete ignition of portions of each on platinum foil. Try them.

Treat a small portion of the solution with platinum chloride, observing the same conditions as in the case of potassium (‡); compare with the corresponding potassium salt (‡); the two can be distinguished by ignition. Try it.

Work out a method for the separation and detection of potassium, sodium and ammonium; determine its efficiency by the use of a known solution, then ask for an unknown as a further test.

LITHIUM.

Treat a solution of a lithium salt with tartaric acid, as in the case of potassium and ammonium (‡); also with platinic chloride (‡); compare with potassium, sodium, and ammonium.

Add to a concentrated solution of the chloride sodium carbonate (‡); describe the characteristics of the precipitate, its solubility, etc.

Add disodium phosphate to the cold chloride solution (‡); now heat to boiling (‡).

Determine the flame coloration of lithium salts, also the characteristic spectroscopic bands, and describe (‡).

GROUP II.—THE METALS WHOSE SULPHIDES ARE SOLUBLE IN WATER, BUT WHOSE CARBONATES ARE INSOLUBLE.

Those metals which are included in this group are Magnesium, Barium, Strontium, and Calcium—generally known as the alkaline earth metals.

The group reagent is ammonium carbonate; this substance, under proper conditions, completely precipitates the members of the group from solutions containing them. The elements constituting the group exhibit to a considerable degree a gradation in properties corresponding to the variation in their atomic weights; thus the hydrates increase in solubility with increasing atomic weight, while the reverse is true of the sulphates and other salts.

For convenience in making the analytical separations, magnesium is usually treated separately, not being precipitated with the other members of the group. For this purpose advantage is taken of the characteristic tendency of this element to form soluble double salts with the salts of ammonium, which are not precipitated upon the addition of ammonium carbonate. The other elements constituting the group so closely resemble each other that it is difficult to devise a thoroughly satisfactory method for their separation, hence a variety of methods have been suggested, none of which, however, give very complete separations.

MAGNESIUM.

Reactions of the Solid.—Heat small portions of the sulphate, chloride, and carbonate in ignition-tubes, hold a piece of moistened blue litmus paper at the mouth of the tube (‡). Heat portions of any one of these salts on charcoal, using the blowpipe (‡); moisten the mass thus obtained with cobalt nitrate and again heat; note the color of the mass (‡).[1]

Reactions in Solution.—*Use the sulphate or chloride.*

To a neutral solution add sodium hydrate (‡), warm and filter; test the solubility of the precipitate in acids and in ammonium salts (chloride, carbonate) (‡). Repeat, using ammonium hydrate instead of sodium hydrate; filter and save the filtrate for further tests as described below. Try the action of sodium and ammonium carbonates upon magnesium salts, using both concentrated and dilute solutions (‡); in case no precipitation occurs allow to stand for some time (‡).

Repeat each of the above reactions, having first added an excess of ammonium chloride to the magnesium salt solution; note any observed differences in the reactions, and explain.

To a moderately concentrated neutral solution add disodium phosphate (‡). To another portion add, in the order given, ammonium chloride, ammonium hydroxide and disodium phosphate, shake well and let stand (‡); compare the two precipitates. Test the solubility in dilute acids (‡); will ammonia reprecipitate the magnesium salt from these solutions?

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[1] Not a very satisfactory test; the color is so delicate as to be often completely obscured.

Test the filtrate, saved from the treatment with ammonium hydrate above, according to directions just given (‡). What conclusions may be drawn from this as to the completeness of the precipitation of magnesium salts by ammonium hydrate? Explain.

Try the behavior of magnesium salts toward potassium chromate and ammonium oxalate respectively (‡).

Add excess of barium or calcium hydroxide to the magnesium salt solution and warm, filter, add to the filtrate ammonium chloride and ammonium carbonate to remove excess of barium or calcium, filter and examine the filtrate for magnesium (‡). How can magnesium be separated from potassium and sodium? How from ammonium?

BARIUM.

Reactions of the Solid.—Determine the stability of barium salts (barium chloride, sulphate, carbonate, etc.) under the influence of heat (‡).

Try the solubility of barium salts (chloride, nitrate, etc.) in water, in alcohol, and in a mixture of alcohol and ether, by digesting warm, filtering and testing the filtrate for barium (‡).

Heat some barium chloride on the platinum wire in the non-luminous flame (‡); after heating some time moisten the substance left on the wire and test its reaction on litmus paper (‡); repeat, using barium sulphate and barium phosphate (‡).

Reactions in Solution.— *Use the chloride.*

When sulphuric acid is added to a cold solution of a barium salt a white precipitate is obtained (‡); test its solubility in acids, in alkalies and in a concentrated solution of ammonium sulphate (‡); see if the precipitate can be filtered off readily (‡). Repeat, but heat both the barium solution and the sulphuric acid nearly to boiling before adding them together, then allow to stand until most of the precipitate has subsided; can the filtration be now more readily carried out? Boil the sulphate with a solution of sodium carbonate containing a little sodium sulphate; is it changed to carbonate? Heat some of the sulphate on charcoal, using the reducing flame of the blowpipe, place the residue on a silver coin and moisten (‡).

Alkaline carbonates (sodium, potassium, and ammonium carbonates) give precipitates with barium salts (‡). To make the precipitation with ammonium carbonate complete it is necessary to add ammonia and to heat[1]. Why? Try the solubility of the precipitate in dilute acids (‡); heat some of it with a solution of sodium sulphate, then try the solubility as before; what change has taken place?

To a solution of barium chloride add potassium dichromate in slight excess (‡); filter, and to the filtrate add ammonia or sodium acetate (‡). Try the same, using potassium chromate (‡). Test the solubility of the precipitate in acids, including acetic acid, and in alkalies; boil some of it with sodium carbonate, filter and wash, treat with dilute hydrochloric acid (‡).

Treat the solution with ammonium oxalate (‡); try the solubility in water, hydrochloric, nitric, acetic, and oxalic acids (‡).

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[1] If ammonium chloride is present it is necessary to avoid boiling or long-continued heating, as the carbonate is thereby redissolved to some extent.

To a solution of disodium phosphate add barium chloride until the alkaline reaction of the phosphate disappears (‡); what is the appearance of the precipitate? Determine its solubility in acids, including acetic acid; allow some of it to stand in contact with the mother liquid fifteen or twenty minutes; note any change which takes place in the physical properties of the precipitate.

STRONTIUM.

Reactions of the Solid.—Make the flame test for strontium salts, using the chloride (‡); will the sulphate or carbonate give equally good results? Explain. Determine the stability upon heating, as in the case of barium salts.

Test the solubility of strontium salts (chloride, nitrate) in alcohol and in a mixture of alcohol and ether (‡); pour a little of the alcoholic extract in an evaporating-dish and set fire to the alcohol (‡).

Reactions in Solution.—*Use the chloride.*

Treat the solution with sodium and ammonium carbonate respectively (‡); solubility in water and in dilute acids (‡). Boil some of the precipitate with a solution of sodium sulphate; has it been converted into the sulphate? Give proofs.

To a cold solution of a strontium salt add dilute hydrochloric acid to slightly acid reaction, and then dilute sulphuric acid (‡); describe the precipitate; allow it to stand some time in contact with the liquid (‡). To a portion of the precipitate add ammonium carbonate and allow to stand about twelve hours; what change has taken place? To another portion add a mixture of sodium carbonate and sodium sulphate and boil for thirty minutes; what is obtained? Determine the solubility of strontium sulphate by diluting the strontium chloride with increasing amounts of water before the addition of the sulphuric acid (‡).

Test the behavior of strontium salts when treated with alkaline chromates and dichromates respectively (‡); also the latter in the presence of sodium acetate (‡); compare with barium. If a precipitate is obtained in either case, boil it with sodium carbonate and prove that it has been transformed into the carbonate (‡).

Add to a strontium solution some oxalic acid (‡), filter and to the filtrate add ammonia until the reaction is neutral or slightly alkaline (‡); explain. Repeat the above, using ammonium oxalate instead of oxalic acid (‡); note any differences in the two cases.

Disodium phosphate gives with strontium salts a voluminous white precipitate, which on standing becomes crystalline (‡). Determine its solubility in acids, including acetic acid (‡).

CALCIUM.

Reactions of the Solid.—Describe the flame test for calcium. Try the solubility of calcium salts (chloride, nitrate) in alcohol and in a mixture of alcohol and ether (‡); compare with barium and strontium.

Reactions in Solution.— *Use the chloride.*

To a cold solution add sodium carbonate in sufficient quantity for complete precipitation (‡); filter at once and wash thoroughly to remove any sodium carbonate which may be present (‡); try the reaction of the moist precipitate on litmus paper (‡). Repeat the above, using a slight excess of sodium carbonate, heat the precipitate in contact with the liquid, filter, wash and again test as before (‡).[1]

In dilute solutions of calcium salts sulphuric acid produces no precipitate (‡). Try the test with concentrated solutions (‡); test the solubility of this precipitate in water, dilute acids and in hot concentrated ammonium sulphate (‡). Treat some of the precipitate with ammonium carbonate and allow to stand for twelve hours (‡). Boil some for thirty minutes with a mixture of sodium sulphate and sodium carbonate (‡).

To a moderately dilute solution add oxalic acid or ammonium oxalate (‡). Try the solubility of the precipitate in water, dilute mineral acids and in acetic and oxalic acids (‡). Compare with barium and strontium.

Mix calcium oxalate with solutions of neutral chlorides or nitrates of the heavy metals (copper chloride, silver nitrate, lead nitrate, etc.) and allow to stand in a warm place for an hour; filter and test the filtrate for calcium (‡).

Heat the dried calcium oxalate in a crucible for some time (thirty minutes) (‡).

What is observed on treating calcium salts with potassium dichromate? on adding sodium acetate to this? with potassium chromate? Compare with barium and strontium.

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[1] The two reactions given here are intended to illustrate the difference in the solubility of the amorphous and crystalline modifications of calcium carbonate. The amorphous variety, being slightly soluble in water, gives an alkaline reaction. It is evident that all sodium carbonate must be washed out before testing for alkalinity.

Make the spectroscopic tests for calcium, strontium and barium – tabulate (‡).

Work out a method of separation and detection of magnesium, barium, strontium and calcium, and test it by using unknown mixtures of these. Also a method whereby these can be separated from the members of group I.

GROUP III.—METALS WHOSE SULPHIDES OR HYDROXIDES ARE INSOLUBLE IN WATER, BUT ARE SOLUBLE IN COLD DILUTE ACIDS.

The group includes the metals Aluminium, Chromium, Iron, Manganese, Zinc, Cobalt and Nickel.

The general group reagent is ammonium sulphide, which throws out the sulphides of cobalt, nickel, manganese, zinc and *ferrous* iron, and the hydroxides of aluminium and chromium, while *ferric* iron is first reduced to the ferrous condition and then precipitated as sulphide.

Since the group embraces a number of metals of somewhat different characteristics, for purposes of analytical classification they are best arranged in subdivisions as follows:

DIVISION A.—*Aluminium, Chromium and Ferric Iron.*

The characteristics of the division are: weak basic action; the salts of the weak acids, e.g. carbonic, hydrosulphuric, acetic, hydrocyanic, etc., throw out hydroxides or basic salts of these metals; they are therefore precipitated as hydroxides by treatment with barium carbonate, or (with the exception of chromium) as basic salts, by boiling with sodium acetate.

Division B.—*Manganese, Zinc and Ferrous Iron.*

Characterized by the tendency to form double salts with ammonium compounds; are precipitated as sulphides by ammonium sulphide, which precipitates are easily soluble in dilute acids. Carbonates and acetates do not act as with Division A.

Division C.—*Cobalt and Nickel.*

The presence of rather small quantities of dilute acids will prevent the precipitation of these by hydrogen sulphide, but their sulphides are but slightly soluble in dilute acids *after* precipitation.

ALUMINIUM.

Reactions of the Solid.—Heat aluminium sulphate or chloride in an ignition-tube; test the escaping gas with moistened litmus paper (‡). Heat some of the salt on charcoal before the blowpipe (‡); moisten the mass with a few drops of a solution of cobalt nitrate and again heat sharply; color of the mass (‡).

Reactions in Solution.—*Use the sulphate or chloride.*

Reaction of the solution upon litmus (‡); explain. Treated with ammonium hydroxide, a precipitate is obtained (‡); test its solubility in excess of the reagent, in ammonium salts, in dilute acids and in alkaline hydroxides (‡).

Add sodium hydroxide to the solution (‡); behavior in excess of the reagent (‡); is this changed upon boiling? Try the effect of ammonium salts (e.g., the chloride) upon the solution produced by the addition of the sodium hydroxide (‡); boil this solution (‡).

In the above cases add some organic acid (e.g., tartaric, oxalic, citric, etc.) to the solution *before* treating with the alkali (‡); from the result noted what conclusions may be drawn as to the precautions necessary to insure complete precipitation of aluminium as hydroxide?

To the solution add ammonium or sodium carbonate (‡); is the precipitate soluble in excess of the reagent, in alkalies, in dilute acids?

To a cold solution of aluminium chloride (why not the sulphate?) add freshly precipitated barium carbonate,[1] allow to stand an hour and examine the composition of the precipitate (‡); determine the completeness of the precipitation (‡). If not complete, allow to stand in contact with the barium carbonate for twelve hours with occasional stirring, then filter and test the filtrate for aluminium (‡).

Pass hydrogen sulphide into the solution (‡). Repeat, using a solution of ammonium sulphide (‡); what is the composition of the precipitate?

Neutralize a solution of aluminium sulphate by adding sodium carbonate until a faint permanent precipitate appears, filter, add sodium acetate in slight excess, dilute with water and boil the solution (‡), filter hot and test the filtrate for aluminium (‡).

Add disodium phosphate in small amount to the aluminium solution (‡); test the solubility in ammonium hydroxide, sodium hydroxide, acetic acid, and in dilute mineral acids (‡). Would it be possible to reprecipitate from this latter solution by using sodium acetate?

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[1] The barium carbonate used should be freshly prepared. This can be best done by treating barium chloride with ammonium carbonate, filtering and washing by decantation until the precipitate is free from chlorides. Place the barium carbonate thus prepared in a flask, add water and shake until a cream is formed; use this for the precipitation.

CHROMIUM.

Reactions of the Solid.—Prepare a bead of borax or of microcosmic salt by fusing in the loop of a platinum wire; while still hot touch it to a small quantity (about the size of a pin-point) of a chromium salt and then heat to fusion, using first the oxidizing and then the reducing flame of the burner; note the color imparted to the bead in each case (‡).

Fuse on platinum foil or in a small crucible a mixture of the following: Sodium carbonate two parts, potassium nitrate one part, and one part of chromium salt (‡). What proof can be furnished as to the product of the reaction?

Reactions in Solution.—*Use the sulphate or chloride.*

Treat the solution with ammonium hydroxide (‡); solubility in excess of the reagent (‡). Is the precipitate soluble in acids? Repeat the above, using sodium hydrate (‡). Is the precipitate soluble in excess of the reagent? Treat a portion of this last with ammonium chloride solution (‡); boil another portion for some time (‡). Is this last precipitate (after cooling) again soluble in excess of sodium hydrate?

Make a mixture of a chromium and zinc salt in solution, then treat as before in the cold with sodium hydroxide in excess, filter, wash the precipitate and determine the presence or absence of chromium in it by the bead test (‡).[1]

Add freshly precipitated barium carbonate (chromium chloride should be used for this test), set aside without heating for twelve hours; filter and test the filtrate for chromium (‡).

What is formed on treating the solution with hydrogen sulphide? with ammonium sulphide? Solubility in acids (‡).

Add sodium acetate in slight excess to the chromium solution, dilute and boil (‡); compare with aluminium.

Make some chromium hydroxide by the first method given; allow to settle and pour off as much of the liquid as possible. To the precipitate add concentrated nitric acid and heat, and to the hot solution add *small* pieces of potassium chlorate (this should be done under the hood); continue until the solution becomes brown. Explain. Pour a little of this solution into water, neutralize with ammonium carbonate and test with solutions of barium chloride, lead acetate, silver nitrate, etc. (‡). Repeat, by shaking the chromium hydroxide up with a little water, adding sodium peroxide and heating (‡). Make tests as before (‡).

Reactions for Chromic Acid.—*Use potassium chromate.*[2]

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[1] This shows that little reliance can be placed upon the solubility of chromium hydroxide in sodium hydroxide for purposes of separation, since here both the chromium and zinc hydroxides should be soluble, as they are, when treated separately with excess of sodium hydroxide, yet when mixed they do not go completely into solution. It is impossible to separate chromium from other metals by this means.

[2] These are given here instead of under the acids, because they must of necessity be studied in connection with the basic properties of the metal, both being used for its characterization.

To separate portions of the chromate add solutions of barium chloride, lead nitrate, mercurous nitrate, bismuth nitrate, and silver nitrate, respectively (‡). Test the solubilities of these precipitates in acids and in alkalies (‡).

The chromates are good oxidizing agents; the following reactions show this: Treat a concentrated solution with concentrated hydrochloric acid, boil and then add alcohol; odor (‡), color (‡), reaction (‡). Pass hydrogen sulphide into an acidulated solution of a chromate or dichromate (‡); repeat, using ammonium sulphide (‡). Would chromium if present originally only in the form of chromic acid or a chromate be also found as a base during the qualitative separation? Explain.

IRON.

Ferric Salts.

Reactions of the Solid.—Heat portions of the chloride or sulphate in ignition-tubes (‡); test the escaping gas with moistened litmus paper (‡). Repeat, using a crucible instead of the ignition-tube, heating to the highest attainable temperature with the burner; is the residue readily soluble in acids?

Heat some of the salt in a borax or microcosmic salt bead, using both the oxidizing and reducing flames (‡).

Reactions in Solution.—*Use the chloride.*

Add, with constant shaking, sodium carbonate until a slight permanent precipitate is obtained, filter and use the solution, now free from uncombined acids, for the following tests: To separate portions of the solution add sodium hydroxide and ammonium hydroxide (‡); solubility in excess of the reagent and in dilute acids (‡). Try what effect the presence of organic acids (e.g. tartaric, oxalic, etc.) has on the above precipitation (‡). Filter off some of the precipitate, wash with hot water, then place the filter and precipitate together in a crucible, heat gently until the precipitate is dry, then raise the temperature gradually until the paper is burned and finally heat for fifteen or twenty minutes at as high a temperature as possible using the blast-lamp (‡); determine the solubility of the ignited precipitate in acids, dilute and concentrated (‡).

Add freshly precipitated barium carbonate (‡); allow to stand twelve hours, filter and test the filtrate for iron (‡).

Pass hydrogen sulphide into the solution (‡); add ammonium hydroxide (‡). Treat some of the solution with ammonium sulphide (‡); distinction from aluminium and chromium.

To the neutral solution add sodium acetate in excess and a few drops of acetic acid (‡); dilute largely with water, boil and filter hot (‡); test the filtrate for iron (‡). Compare with aluminium and chromium. Repeat the above, using very little of the ferric chloride, but with the addition of a few drops of disodium phosphate; test the filtrate, after boiling and filtering as before, for iron and phosphoric acid (‡). Could phosphoric acid or a soluble phosphate be removed from the solution by this means?

To separate portions of the iron solution add potassium sulphocyanate, potassium ferrocyanide, and potassium ferricyanide (‡). To a few cubic centimeters of a very dilute solution of the first add a little ether and shake (‡), then add cautiously—drop by drop—potassium ferrocyanide, shaking after each addition (‡). To separate portions of the second add hydrochloric acid and sodium hydroxide and heat (‡); solubilities (‡).

Try the action of reducing agents—e.g. zinc and hydrochloric acid, stannous chloride, sodium sulphite, sodium thiosulphate, potassium iodide, etc.—on the solution (‡). After the action in each case test for ferric salts (‡).

Outline a method for the separation and detection of aluminium, chromium and iron and determine its efficiency.

Ferrous Salts.

Reactions of the Solid.—Make the bead test, using ferrous salts (sulphate, chloride) (‡). Heat crystallized ferrous sulphate in a porcelain crucible at a moderate temperature (‡), then ignite at a high temperature (‡); test the escaping gases with moistened litmus paper.

Reactions in Solution.—Prepare a solution for use as follows: Treat iron turnings or filings with dilute hydrochloric acid and heat to boiling. When the action has nearly ceased cork the vessel and use without filtering, by decanting the liquid as needed from the undissolved filings.

Treat with sodium hydroxide and ammonium hydroxide respectively (‡); allow one portion of each to stand (‡); test the solubility of the other portion in excess of the reagent (‡); effect of heat upon this (‡). Repeat the above, adding in each case ammonium chloride before treating with the alkalies (‡).

Try the reaction of carbonates, including barium carbonate, upon the solution (‡); compare with ferric salts.

Pass hydrogen sulphide into the nearly neutral solution (‡); into the acid solution (‡). Add ammonium sulphide (‡); determine the completeness of the precipitation, also what effect the previous addition of ammonium chloride has upon this (‡). Allow the precipitate to stand (‡); test its solubility in acids and in alkalies (‡).

Test portions of the solution with potassium sulphocyanate, potassium ferrocyanide and potassium ferricyanide; note any difference in behavior as compared with ferric compounds (‡). Allow the ferrocyanide precipitate to stand exposed to the air for an hour or so (‡). Explain.

Add sodium acetate in excess, dilute and boil (‡). Add oxalic acid to a solution of the ferrous salt (‡); filter, wash and dry the precipitate, transfer it to a porcelain crucible and heat (‡).

The following reactions illustrate the oxidation of ferrous salts. Boil a neutral solution of ferrous sulphate (‡). Add concentrated nitric acid to the solution and boil (‡). Add concentrated hydrochloric acid, heat, then add two or three small crystals of potassium chlorate (‡). Acidify the solution, then add potassium permanganate, a little at a time, until a faint permanent coloration is obtained (‡). Prove that a ferric salt is formed in each case.

From the reactions studied how could both ferric and ferrous compounds be detected when together in solution? How could they be separated?

MANGANESE.

Reactions of the Solid.—Make the bead test for manganese, using both the oxidizing and the reducing flame (‡).

Mix some manganese salt with a little dry sodium carbonate or hydrate and potassium nitrate, fuse the mixture on platinum foil (‡). Dissolve the fused mass in water, add acetic acid in slight excess and heat to boiling (‡).

Reactions in Solution.—*Use the sulphate or chloride.*

Add sodium hydroxide (‡); divide the precipitate into two parts; to one add ammonium chloride in excess (‡), let the other stand exposed to the air (‡); after the change has taken place in the latter case, add oxalic acid (‡). What change is observed? What takes place on heating the mixture?

Add ammonium hydroxide to neutral and acid solutions respectively (‡); allow both to stand (‡). Explain.

Treat with sodium and ammonium carbonate respectively, varying the conditions as above (‡). Try the effect of hydrogen sulphide upon the manganese salt solution (‡). Treat with ammonium sulphide in slight excess (‡); filter, does the filtrate contain manganese? Try the solubility of the precipitate in ammonia, ammonium chloride, and in dilute acids, including acetic acid (‡) (the precipitation of manganese as sulphide is not complete unless ammonium chloride is present; prove this).

To the solution add ammonium chloride, ammonium hydroxide and disodium phosphate (‡) (cf. magnesium); change on standing (‡).

Treat about a gram of minium (Pb_3O_4) in a test-tube with twice its volume of nitric acid, specific gravity 1.20-1.30, and heat nearly to boiling; add two or three drops of a very dilute solution of a manganous salt; let the mixture stand until the solid matter has settled (‡) (the presence of chlorine or of chlorides is to be avoided in making this test, though if quite dilute the reaction will take place sufficiently to give the characteristic color).

ZINC.

Reactions of the Solid.—Heat a zinc salt (chloride or sulphate) in a porcelain crucible at a moderately high temperature (‡); test the escaping gas with moistened litmus paper (‡). Heat some of the salt on charcoal, using the blowpipe; note the color of the mass while hot and upon cooling (‡). Moisten the residue with a few drops of cobalt nitrate solution and again heat (‡).

Reactions in Solution.—*Use the sulphate.*

Treat the solution with sodium hydroxide (‡); add the reagent in excess (‡); does any change take place upon boiling? Repeat, using ammonium hydroxide (‡). Note any difference between zinc, aluminium and chromium when treated in the manner above described. Try the solubility of the above precipitates in ammonium chloride (‡).

Add sodium carbonate and ammonium carbonate respectively (‡), then an excess of each (‡). Does ammonium chloride prevent the precipitation in these cases?

Treat the solution with hydrogen sulphide and ammonium sulphide respectively (‡); test the solubility of the precipitate obtained in ammonium chloride, in potassium cyanide and in dilute acids, including acetic acid (‡). Add sodium acetate to a solution of a zinc salt, then pass hydrogen sulphide into the solution (‡).

Prepare a plan for separating and distinguishing between ferrous iron, manganese and zinc, and prove its efficiency.

NICKEL AND CABOLT.

NOTE.—The reactions of nickel and cobalt are so similar in character that it is thought the slight differences observed between them will be best brought out by considering them together. The student is directed, unless otherwise stated in the following cases, to treat the cobalt and nickel solutions alike, noting any differences in behavior.

Reactions of the Solid.—What effect has heat upon the salts of nickel and cobalt? Make the bead test for both salts, noting any differences shown in the oxidizing and reducing flame (‡).

Reactions of the Solution.—*Use the chlorides, nitrates or sulphates.*

Treat with sodium hydroxide (‡); try the solubility in ammonium salts and dilute acids (‡). Try the action of an excess of the alkali, also the action of heat (‡). Repeat, using ammonium hydroxide (‡); add excess of the reagent (‡). Does sodium hydroxide throw down a precipitate from these solutions? Try the behavior of the carbonate under similar conditions (‡).

Pass hydrogen sulphide into neutral and acid solutions of nickel and cobalt salts (‡). Treat with ammonium chloride and ammonium sulphide in slight excess, place in a stoppered flask, allow to stand a half-hour with occasional shaking (‡), filter and wash the precipitate.[1] Test the solubility of the precipitate in dilute and concentrated acids and in aqua regia (‡).

(Poison.—*Use the hood.*) Add potassium cyanide, at first in small quantity (‡), then in just sufficient excess to effect solution (‡); treat a portion of the cold solution thus obtained with hydrochloric acid (‡); to another portion add two or three drops of dilute hydrochloric acid and digest warm for fifteen or twenty minutes; cool and again treat with acid (‡). Note any difference in the behavior of nickel and cobalt. Explain.

Add just sufficient excess of potassium cyanide to redissolve the precipitate first formed, then add a little sodium hydroxide and bromine water until the solution shows the color of the bromine; allow the solution to stand for a few minutes (‡).

Acidify with acetic acid, add potassium nitrite in excess, warm to 30°—40° C. and allow the solution to stand (‡).

To the solutions add a few drops of a saturated solution of alum, neutralize with ammonium hydroxide, add potassium ferricyanide, and shake (‡); to the precipitate add strong ammonium hydroxide (‡).[2]

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[1] The sulphide of nickel is somewhat soluble in ammonium sulphide, imparting a dark color to the filtrate; the use of potassium sulphide avoids this.

[2] See Browning and Hartwell, Chemical News, 82, 208.

Prepare a scheme for the separation and detection of all the bases of group III; test its applicability by the use of unknowns.[1]

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[1] For the treatment of this group when phosphates, oxalates or the salts of other organic acids are present the student is referred to some one of the standard text-books upon qualitative analysis.

DIVISION II.

METALS WHOSE SULPHIDES ARE INSOLUBLE IN DILUTE ACIDS.

GROUPS IV AND VI.—METALS WHOSE SULPHIDES ARE INSOLUBLE IN WATER, IN DILUTE ACIDS AND IN THE ALKALINE SULPHIDES; AND (GROUP VI) WHOSE CHLORIDES ARE INSOLUBLE IN WATER.

The metals which fall under the classification given above are Mercury, Lead, Silver, Copper, Cadmium and Bismuth: their properties are so various and differ so markedly from each other (being different for the same element in its several states of valence) that several methods of classification and separation suggest themselves. They possess however in common the property of being precipitated as sulphides in an acid solution by hydrogen sulphide, which therefore constitutes the group reagent. Since, however, the same reagent precipitates the salts of other metals under similar conditions a further distinction is made, based upon the insolubility of the sulphides of these, and the solubility of the sulphides of the others (see group V), in the sulphides of the alkalies (the sulphides of copper and mercury are however somewhat soluble). The salts of two of these (mercury, bismuth) are more or less easily decomposed by water, forming basic compounds; and of all (less readily in the case of the halogen salts) are quite generally decomposed by heat, yielding either an oxide of the metal or the metal itself (in the case of mercury).

The three elements constituting group VI, silver, lead and univalent mercury, while in general exhibiting properties similar to those of the other metals here mentioned, differ in that their halogen salts are practically insoluble in water. This difference is for the sake of convenience utilized for purposes of separation, thus constituting a separate group—known usually as the hydrochloric acid group, that acid being used as the group reagent. Because of the fact that lead is not completely separated as the chloride, and that both silver and mercury exhibit analogies to the members of group IV, a separate consideration of these metals under the group designation seems inadvisable.

MERCURY.

Reactions of the Solid.—Test the solubility of the metal in acids, dilute and concentrated, hot and cold (‡). Determine the solubility of the mercurous and mercuric salts in water, alcohol and dilute acids (‡). Determine the stability of the salts when heated (use the chlorides, nitrates, sulphates, oxides, etc.) (‡); repeat, after mixing the salts with dry sodium carbonate (‡).

Mercuric Compounds.

Reactions in Solution.—*Use the nitrate or chloride.*

Treat with sodium hydroxide (‡); solubility in excess of reagent and in acids (‡). Repeat, using ammonium hydroxide, also ammonium carbonate (‡).

Pass hydrogen sulphide into the solution (‡); note change in color on continued action of the hydrogen sulphide (‡).[1] Determine the influence of acids, both concentrated and dilute, upon the completeness of the precipitation (‡); test the solubility of the precipitate in hot and cold acid, in aqua regia and in potassium cyanide (‡).

What is observed on treating the solution with potassium iodide? Solubility in excess of each of the reagents (‡), in water and in alcohol (‡).

Mercurous Compounds.

Reactions in Solution.—*Use the nitrate.*

Add sodium hydroxide (‡), warm gently (‡). Repeat, using ammonium hydroxide, also ammonium carbonate (‡); action of an excess of the precipitant (‡); solubility in acids (‡).

Pass hydrogen sulphide into the solution (‡); boil with dilute nitric acid, also with aqua regia (‡).

Treat with dilute hydrochloric acid or a soluble chloride (‡); try the solubility of the precipitate in water, in dilute acid, in ammonia, and in hot nitric acid (‡).

To separate portions of the solution add potassium iodide, potassium chromate, potassium dichromate and potassium cyanide (‡). In each case determine the solubility in excess of the precipitant, in acids and in alkalies.

Treat solutions of mercuric and mercurous salts respectively with stannous chloride (‡); effect of an excess of the stannous chloride and warming (‡).

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[1] This precipitate is somewhat soluble in alkaline sulphides, from which solution the mercuric sulphide may be precipitated by the addition of ammonium chloride.

How can mercuric and mercurous salts be distinguished and separated when both are present?

LEAD.

Reactions of the Solid.—Heat the higher oxides of lead (Pb_3O_4, PbO_2) to a moderately high temperature; into what are they converted?

Heat lead salts (nitrate, carbonate) in an ignition-tube (‡); what gases are given off? Mix with sodium carbonate and repeat, heating on charcoal, using the blowpipe (‡); character of button and color of incrustation (‡).

Reactions in Solution.—*Use the nitrate or acetate.*

Add sodium hydroxide (‡); effect of an excess of the reagent (‡). Does ammonium hydroxide act similarly?

What is the effect of alkaline carbonates upon lead salts? Try the solubility of the precipitate in alkalies and in acids (‡).

Pass hydrogen sulphide into the solution (‡); solubility in alkalies and in acids (‡).

Treat with dilute hydrochloric acid (‡); pour off the liquid, add water in considerable excess and boil (‡); filter and allow the filtrate to cool (‡); is the precipitate soluble in alkalies and in ammonia? Repeat the above, using sulphuric acid (‡); try the solubility as before (‡), also in boiling ammonium acetate[1] and ammonium tartrate solution (‡); pass hydrogen sulphide into these (‡).

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[1] J. C. Long, *Amer. Chem. Jour.*, **22**, 217, has observed that the best concentration for the ammonium acetate is a 33% solution, using about 10 cc. for each gram of $PbSO_4$.

Add potassium iodide (‡); treat the precipitate with a little acetic acid, dilute largely with water and boil (‡). What is observed on cooling the solution?

Treat with potassium chromate (‡); to one portion of the precipitate add sodium hydroxide in excess (‡); to another add a *small amount* of sodium hydrate or ammonium hydrate and warm (‡); to a third portion add dilute nitric acid and heat (‡).

SILVER.

Reactions of the Solid.—Heat a small piece of silver nitrate mixed with sodium carbonate on charcoal before the blowpipe (‡); compare the button obtained with others studied, also determine its solubility in nitric acid (‡).

Reactions in Solution.—*Use the nitrate.*

Treat with sodium hydroxide, very dilute ammonium hydroxide and ammonium carbonate respectively (‡); solubility in excess (‡). Does the presence of an acid affect the precipitation in any of the preceding cases? Explain.

Treat with hydrochloric acid (‡); separate into two parts; filter one and allow the precipitate to stand exposed to the light (‡); treat the other with ammonia in excess (‡). Effect of dilute nitric acid when added in excess to the ammoniacal solution (‡)

Perform the same operation, using solutions of potassium bromide, potassium iodide and potassium cyanide respectively, instead of the hydrochloric acid (‡).

Pass hydrogen sulphide into the solution (‡); solubility in alkalies, alkaline sulphides, ammonia, potassium cyanide, and in acids (‡).

Determine the action of disodium phosphate, potassium chromate, and potassium dichromate respectively on silver salts (‡); solubilities (‡).

Reduction Reactions.—Treat the solution with ferrous sulphate, sodium sulphite, sodium thiosulphate, and sodium phosphite respectively (‡). In cases where no reaction is observed boil the solution.

Prepare a plan for the separation of silver, lead and mercurous salts.[1]—*Group VI.*

COPPER.

Reactions of the Solid.—Try the solubility of the metal in concentrated and in dilute acids, both cold and hot (‡).

Heat a copper salt mixed with sodium carbonate on charcoal in the reducing flame (‡). Make the flame[2] and bead tests for copper (‡).

Reactions in Solution.—*Use the sulphate.*

Upon adding sodium hydroxide a precipitate is obtained (‡); add excess of the alkali and boil (‡).

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[1] Attention is called to the fact that where ammonia is used to effect the separation of the chlorides of silver and of mercury, frequently considerable amounts of undissolved silver chloride are held back by the black mercurous compound formed. Sometimes, where silver is present in small amount, on account of this action, it may entirely escape detection. For the mode of procedure in such cases see Comptes Rendus, 130, 248; Wells' Qualitative Analysis, first edition, page 7, or Fresenius' Qualitative Analysis (1897), page 235.

[2] The flame test for copper varies with the salt, the halogen salts imparting a different color to the flame from that shown by salts of the other acids. See Newth's Manual of Chemical Analysis (1898), page 84.

To a solution of copper sulphate add a slight excess of tartaric acid, then sodium hydroxide (‡); to this add a small amount of dextrose and boil (‡). Explain the application of this reaction in the examination of sugars and in urine analysis.

Treat with ammonium hydroxide, added very cautiously (‡); effect of excess of ammonia (‡). Add potassium cyanide to this (‡); can the presence of copper in the latter solution be readily detected?

Try the action of both sodium and ammonium carbonate upon copper salts (‡).

Pass hydrogen sulphide into a dilute acid solution of the salt (‡); solubility in hot and cold acids, in potassium cyanide, in alkalies, and in alkaline sulphides (‡).

Treat with potassium cyanide (‡); an excess of the cyanide produces what change? Pass hydrogen sulphide into this solution (‡).

Treat with potassium ferrocyanide (‡); try the solubility in acids and in alkalies (‡). Determine the sensitiveness of the ferrocyanide reaction by using very dilute solutions of the copper salt (‡);[1] compare with the ammonia reaction as regards sensitiveness.

Add potassium iodide in slight excess (‡), then add sodium thiosulphate until the color is destroyed (‡); can the copper be entirely precipitated in this way?

CADMIUM.

Reactions of the Solid.—Heat a cadmium salt mixed with sodium carbonate on charcoal; is a button obtained? Describe the color of the incrustation (‡).

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[1] This can be done very readily by bringing a drop of each upon a porcelain plate and allowing them to mix, noting the color produced.

Reactions in Solution.—*Use the sulphate or chloride.*

Treat with sodium hydroxide (‡); solubility in excess of the alkali and in acids (‡).

Repeat, using ammonium hydroxide (‡); solubility in excess (‡); does sodium hydroxide reprecipitate the cadmium from this solution?

Try the action of alkaline carbonates on cadmium salts (‡).

Pass hydrogen sulphide into the solution (‡); solubility of the precipitate in ammonium hydroxide, in ammonium sulphide, in potassium cyanide and in dilute acids (cold and hot) (‡).

Add potassium cyanide (‡); an excess of potassium cyanide produces what effect? Pass hydrogen sulphide into this solution (‡) (distinction from copper).

Treat with potassium iodide (‡); is iodine liberated? Compare with copper.

BISMUTH.

Reactions of the Solid.—Heat a bismuth salt mixed with sodium carbonate on charcoal (‡). Compare with lead (‡); character of the button and incrustation (‡).

Test the solubility of bismuth nitrate in water (‡); repeat, first acidifying the water with nitric acid (‡).

Reactions in Solution.—*Use the nitrate.*

Pour a solution of the nitrate into a large volume of water (‡). Treat another portion with sodium chloride, evaporate until most of the free acid has been removed, then pour into water (‡); filter and test filtrate for bismuth (‡). Determine the delicacy of this reaction (‡).

Treat the solution with alkalies and with ammonia (‡);

solubilities of the precipitates (?). Repeat, using the alkaline carbonates (?).

Pass hydrogen sulphide into the weakly acid solution (?); solubility of the precipitate in ammonium sulphide, in potassium cyanide and in acids (hot and cold) (?).

Add potassium dichromate (?); try the solubility in nitric acid and in sodium hydroxide (?) (distinction from lead).

To a small amount of stannous chloride, add sodium hydroxide until the precipitate first formed (?) is dissolved (?), then add the bismuth nitrate solution little by little (?); delicacy of the reaction (?).

Prepare a scheme for the separation of bivalent mercury, lead, copper, cadmium and bismuth, and determine its efficiency by experiment.

GROUP V.—METALS WHOSE SULPHIDES ARE INSOLUBLE IN DILUTE ACIDS, BUT DISSOLVE IN THE ALKALINE SULPHIDES.

The metals included in this list are Tin, Antimony, Arsenic, Gold and Platinum. They are all precipitated by hydrogen sulphide from neutral or weakly acid solutions, and their sulphides dissolve on treatment with alkaline sulphides (more readily on the addition of sulphur), yielding soluble "thio" salts, in which these metals act as acid radicals. The metals gold and platinum, however, exhibit properties somewhat different from those of tin, antimony and arsenic, hence for convenience the group is subdivided as follows:

Division A.—*Tin, Antimony, Arsenic.*

These metals form stable oxides when ignited, which have acid properties; their chlorides do not suffer decomposition under similar conditions, but volatilize; their sulphides (with the exception of the sulphides of arsenic) are soluble in hot hydrochloric acid.

Division B.—*Gold, Platinum.*

These metals are characterized by the readiness with which their salts suffer reduction; on ignition they are decomposed, yielding the metal; their chlorides also exhibit this property, decomposing into the metal and chlorine; their sulphides are almost insoluble in hot hydrochloric acid and are not readily soluble in the alkaline sulphides, hence they are commonly removed by reduction to the metal.

TIN.

Reactions of the Solid.—Treat the metal with acids (e.g., hydrochloric, nitric and sulphuric) dilute and concentrated, both in the cold and on heating; note the character of the reaction in each case and determine what gases are given off (‡).

Heat a compound of tin mixed with sodium carbonate and potassium cyanide (‡) on charcoal, using the reducing flame of the blowpipe (‡); characteristics of the button (‡); color of incrustation (‡). Moisten this with cobalt nitrate and reheat (‡); compare with zinc.

Stannous Salts.

Reactions in Solution.— *Use the chloride.*

Treat with sodium and ammonium hydroxides respectively (‡); solubility in excess of the precipitant (‡). Repeat, using the carbonates (‡).

Treat with hydrogen sulphide (‡). Determine the best conditions for precipitation by using (1) a neutral solution, (2) a weakly acid solution and (3) a strongly acid solution (‡). Solubility of the precipitate in acids cold and hot, in alkalies, in alkaline carbonates, in colorless ammonium sulphide, and in yellow ammonium sulphide (‡). Add dilute acid to any one of these in which solution occurs (‡).

Reduction Reactions.—Add stannous chloride in small quantity, and in excess respectively, to solutions of the following substances: ferric chloride, mercuric chloride, copper sulphate, potassium permanganate and potassium chromate; describe what takes place in each case and give your method of proof (‡).

To a solution of stannous chloride in sodium hydrate add bismuth nitrate (‡) (see under bismuth .

Stannic Salts.

Reactions in Solution.— *Use the chloride.*

Alkalies, alkaline carbonates and ammonia produce what effect? Solubility in excess (‡); also determine the solubility in acids (‡)[1].

Treat with hydrogen sulphide and determine the solubilities of the precipitate as in the case of stannous salts (‡).

To the solution (which should be neutral) add respectively sodium sulphate solution and dilute sulphuric acid (‡) (distinction from stannous salts).

The following reactions are common to both stannous and stannic salts: Insert slips of zinc into either the acid solution, or a solution of the tin salt in excess of alkali (‡); determine the solubility in hot dilute hydrochloric acid (‡); if soluble, add a solution of mercuric chloride (‡).

ANTIMONY.

Reactions of the Solid.—Heat any antimony compound in the dry state, mixed with sodium carbonate and potassium cyanide on charcoal (‡); compare the button with others which have been obtained (‡); color of incrustation (‡). Are the fumes possessed of any characteristic odor? Compare with arsenic.

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[1] The precipitate obtained by treating stannic salts with alkalies is similar to that obtained by treating the metal with concentrated nitric acid; the former is known as *stannic acid* (H_2SnO_3) and the latter as *meta-stannic acid* $(H_2SnO_3)_x$. The solubilities of the latter should be compared with those of the former. (See also R. Lorenz, Zeitsch. f. Anorg. Ch., IX. 369.)

Antimonious Compounds.

Reactions in Solution.—*Use a solution of the oxide* (Sb_2O_3) *or trichloride in hydrochloric acid.*

Pour a small amount of the not too acid solution into a considerable quantity of water (‡); repeat, having previously added tartaric acid to the antimony solution (‡); how do bismuth salts behave under similar conditions?

Treat with alkalies, alkaline carbonates, and ammonia respectively (‡); solubility in excess, also in acids (‡).

Add hydrogen sulphide to the solution (‡); determine the conditions of complete precipitation (‡). Solubility of the sulphide in acids (cold and hot); in alkalies, in alkaline carbonates, and in both the colorless and yellow ammonium sulphide (‡); effect of adding acids to the solutions obtained in any of these cases (‡).

Add silver nitrate to an alkaline solution of the antimony salt (‡); treat the product with ammonia in excess; does the precipitate completely dissolve? Treat with potassium iodide and heat (‡).

Antimonic Compounds.

Reactions in Solution.—*Use a solution of the pentachloride in hydrochloric acid.*

Treat with alkalies, alkaline carbonates and ammonia respectively (‡).

Pass hydrogen sulphide into the solution (‡); solubilities of the precipitate (‡).

Add silver nitrate to a solution of potassium or sodium antimoniate (‡); treat the product with ammonia (‡); (distinction from antimonious compounds).

Treat the solution with potassium iodide and heat (‡) (distinction from antimonious compounds).

The following reactions are common to all compounds of antimony: To an acidified solution add zinc and a strip of platinum foil (‡) (compare with tin); treat the deposit with a drop of concentrated nitric acid (‡), also determine its solubility in hot dilute hydrochloric acid (‡) (compare with tin).

ARSENIC.

Reactions of the Solid.—Heat oxide of arsenic mixed with sodium carbonate on charcoal (‡); note behavior, incrustation and odor of fumes (‡); compare with antimony. Heat some of the oxide in a *dry* test-tube (‡).

Mix some of the arsenic compound with sodium carbonate and potassium cyanide (or use a plug of charcoal) and heat in a small *dry* test-tube or ignition-tube (‡).

Arsenious Compounds.

Reactions in Solution.—*Use a solution of the oxide* (As_2O_3) *in hydrochloric acid.*

Treat the slightly acidulated compound with hydrogen sulphide (‡); will the reaction take place in a neutral or alkaline solution?. Test the solubility of the precipitate in acids (cold and hot), in alkalies, in ammonium carbonate, and in the colorless and yellow ammonium sulphides (‡); action of acid when added to those in which solution is effected (‡).

Add copper sulphate (‡); solubility in ammonia and the alkalies (‡); boil some of the alkaline solution (‡).

Treat a solution of an arsenite (e. g. sodium arsenite) with silver nitrate (‡); solubility in nitric acid and in ammonia (‡); can the solution in either be reprecipitated by adding the other reagent? Boil the ammoniacal solution (‡).

Introduce a strip of clean copper foil into the acidulated solution and warm (‡); dry the foil, place it in a dry test-tube and heat gently (‡). (Reinsch's test.)

Into an alkaline solution of an arsenite introduce a strip of zinc and hold a piece of paper moistened with silver nitrate at the mouth of the tube (‡). (Fleitmann's test.)

Arsenic Compounds.

Reactions in Solution.—*Use sodium arseniate.*

Acidulate and precipitate with hydrogen sulphide (‡); treat the precipitate as under arsenious compounds (‡).

Treat with copper sulphate (‡); solubility in acids and in alkalies (‡); effect of boiling the alkaline solution (‡) (compare with arsenites).

Acidulate slightly with nitric acid then add silver nitrate (‡); solubility in nitric acid and ammonia (‡); boil the ammoniacal solution (‡) (compare with arsenites).

To the solution add ammonium chloride, ammonia and magnesium sulphate (‡) (compare with phosphoric acid); dissolve the precipitate in dilute acid and pass hydrogen sulphide into the solution (‡).

Marsh's Test.—(Caution: *Use the hood, as the gas is extremely poisonous.*)

Fit a small flask with a two-hole stopper, provided with a funnel-tube and outlet-tube; connect with a piece of moderately hard glass tubing, drawn to a point at the end. Put some zinc or aluminum into the flask, add sulphuric acid, and when the flask is completely filled with hydrogen, light the gas at the tip of the pointed tube. Pour in a *small* quantity of an arsenic solution; note change of color of the flame (‡); hold a porcelain dish momentarily in the flame (‡); heat the hard glass tube through which the gas is passing (‡). Try the solubility of the arsenic spots in a solution of bleaching powder, also in concentrated hydrochloric and nitric acids (?). Perform a similar experiment with antimony and compare the two.

Work out a method of separation for tin, antimony and arsenic, and determine its accuracy.

GOLD.

Use a Solution of the Chloride.—Pass hydrogen sulphide into the solution (‡); determine the solubility of the precipitate in dilute and concentrated acids (cold and hot), in aqua regia, and in both colorless and yellow ammonium sulphides (‡). Do acids reprecipitate from these solutions?

Treat with a solution of ferrous sulphate (‡); solubility of the precipitate (‡). To a nearly neutral solution of the chloride (it should be free from nitric acid) add oxalic acid and warm (‡).

Prepare a mixture of stannic and stannous chlorides and add it to a dilute solution of the chloride of gold (‡); determine the sensitiveness of the reaction.

Many other reducing agents, potassium nitrite, sulphurous acid (on warming), formates, etc., precipitate metallic gold.

PLATINUM.

Use a Solution of Hydrochlor-platinic Acid or of Platinic Chloride.—Pass hydrogen sulphide into both cold and hot solutions (‡)[1]; determine the solubility of this precipitate, using acids and yellow ammonium sulphide (‡).

Acidify the solution with hydrochloric acid, add potassium chloride and excess of alcohol (‡); (if crystals do not readily separate, evaporate the mixture before adding the alcohol). Repeat, using ammonium chloride (‡). Collect some of the crystals in each case, dry and ignite (‡).

Add ferrous sulphate and boil (‡); also stannous chloride (‡). Treat with potassium nitrite and allow to stand for some time (‡).

Try the action of oxalic and sulphurous acids on platinum solutions (‡).

How may gold and platinum be separated?

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[1] This precipitation is not complete, and it has a tendency also to precipitate other metallic sulphides which are themselves soluble in acids, e.g. iron.

PART II.

THE NON-METALLIC OR ACID-FORMING ELEMENTS.

THE NON-METALLIC OR ACID-FORMING ELEMENTS.

Under this designation are included all those elements which are not precipitated by the usual reagents (hydrogen sulphide, ammonium sulphide, ammonium carbonate, etc.). The principal distinction between this class and that previously considered lies in the fact that their oxides are acidic in character, while the oxides of the metallic elements are basic. This distinction is not in all cases sharply drawn, and we find one set frequently encroaching upon the other (e.g. in the case of manganese, chromium, tin, antimony, arsenic, etc.).

The non-metallic elements, though fewer in number than the metallic, are much more difficult of classification, since most of them form several acids, with widely differing properties; an attempt, therefore, to classify them into distinct groups, based upon their analytical reactions, would have the result of placing acids derived from the same element into different groups.

A grouping of the acids may, nevertheless, be made, based upon their behavior toward certain reagents, e.g. silver nitrate, barium chloride, etc., but such a grouping will be found to possess little real analytical significance, and is of value chiefly as a means of preliminary study, for purposes of elimination of certain acids. This method of grouping will therefore be postponed until a study of those special reactions necessary for the identification of the individual acid radicals in their various combinations has been made. This identification may usually be accomplished without a previous group separation; hence, for the purposes of study, it appears better to arrange the acids under the characteristic element in each, and examine each independently. We should then have (omitting the less commonly occurring acids under each head) the following grouping of the more important ones:

THE HALOGEN ACIDS:

a. *The Acids of Chlorine:* hydrochloric, hypochlorous, chloric, perchloric.
b. *The Acids of Bromine:* hydrobromic, bromic.
c. *The Acids of Iodine:* hydriodic, iodic.
d. *The Acids of Fluorine:* hydrofluoric, hydrofluosilicic.

THE ACIDS OF SULPHUR: hydrosulphuric, sulphuric, sulphurous, thiosulphuric.

THE ACIDS OF NITROGEN: nitric, nitrous.

THE CYANOGEN ACIDS: hydrocyanic, hydroferrocyanic, hydroferricyanic, sulphocyanic.

THE ACIDS OF PHOSPHORUS: ortho-, pyro- and metaphosphoric.

THE COMMONER ACIDS OF CARBON: carbonic, acetic, oxalic, tartaric, citric.

The Acids of Silicon: silicic.

The Acids of Boron: ortho-, meta- and tetraboric.

Miscellaneous: Chiefly those compounds of the base-forming elements which have acid properties, e.g. chromic, arsenic, antimonic acids; they have been considered in connection with the same element as a base, hence need not be more than mentioned here.

THE HALOGEN ACIDS: ACIDS OF CHLORINE, ACIDS OF BROMINE, ACIDS OF IODINE, ACIDS OF FLUORINE.

HYDROCHLORIC ACID.

Heat several chlorides (those of mercury, aluminium, magnesium, silver, sodium, calcium, and ammonium), determine their volatility (‡); also their solubility in water (‡).

Treat any of the above with concentrated sulphuric acid and warm (‡). What is given off? How proved?

Use a Solution of Sodium Chloride.—Add silver nitrate in slight excess (‡); allow the precipitate to stand exposed to the light for several minutes (‡). Test different portions of the precipitate by treatment with dilute nitric acid, ammonium hydroxide, potassium cyanide and sodium thiosulphate, respectively (‡); in case the precipitate dissolves, add nitric acid to the solution obtained (‡).

Place some of the precipitate in a small porcelain crucible; insert a piece of zinc, and moisten with dilute sulphuric acid (?); prove that decomposition takes place, and that the chlorine passes into solution (‡).

Treat some of the solution with lead acetate and mercurous nitrate, respectively (‡); solubility of the precipitates in cold and in hot water (‡), dilute nitric acid (‡), ammonium hydroxide (‡) and potassium cyanide (‡).

To distinguish a chloride from a bromide: mix the substance with about twice its weight of potassium dichromate (both in the solid form); place the mixture in a small retort; add concentrated sulphuric acid, and warm ; collect the escaping gases (‡) in ammonium hydroxide (‡); note color of the solution (‡). Acidify the solution slightly with acetic acid, and add a solution of lead acetate (‡). Show that this is a proof that a chloride was originally present.

Prepare chlorine by heating together manganese dioxide and concentrated hydrochloric acid; pass the gas into solutions of ferrous ammonium sulphate, indigo, litmus, mercurous chloride and potassium iodide. Explain the reaction in each case (‡). How would you prove free chlorine in the presence of hydrochloric acid or of chlorides?

HYDROBROMIC ACID.

Treat some solid potassium bromide with concentrated sulphuric acid (‡) (compare with chlorides). How is hydrobromic acid prepared?

Treat a solution of potassium bromide with silver nitrate, lead acetate and mercurous nitrate, respectively, and examine the precipitate obtained in each case as given under chlorides (‡). How do they compare as to solubility with the corresponding chlorides?

Heat together in a retort a mixture of a solid bromide and potassium dichromate, treated with concentrated sulphuric acid (‡); collect the distillate in ammonia (‡) (compare with chlorides).

To a solution of a bromide add a few drops of carbon disulphide, then some chlorine water, and shake (‡); continue the addition of chlorine water and the shaking until the solution becomes colorless (‡). Explain.

Prepare bromine by mixing together potassium bromide and manganese dioxide, and treating with moderately concentrated sulphuric acid; warm, and collect the gas in water. Compare its properties with those of chlorine.

HYDRIODIC ACID.

Heat several iodides (those of potassium, lead, silver and bivalent mercury) in ignition-tubes (‡). Explain.

Treat some crystals of potassium iodide with concentrated sulphuric acid (‡). How is hydriodic acid prepared?

Use a Solution of Potassium Iodide.—Treat with silver nitrate (‡); is the precipitate affected by light? Solubility of the precipitate in nitric acid, ammonia, potassium cyanide and sodium thiosulphate (‡); does nitric acid reprecipitate silver iodide from any of these? Compare with the bromides and chlorides as regards solubility. Will zinc and sulphuric acid effect the decomposition of silver iodide?

Repeat, using lead acetate (‡); solubility in cold and in hot water, in acetic and nitric acids, and in sodium acetate (‡).

Describe the precipitate obtained with mercurous nitrate (‡); is it soluble in ammonia, hot water, or potassium iodide?

Add mercuric nitrate until a precipitate is obtained (‡); to this add potassium iodide in slight excess (‡), then sodium hydrate; appearance of the solution (‡); add to this a few drops of very dilute ammonia solution (‡) (Nessler's test).

To the solution add copper sulphate in excess (‡); color of solution (‡); add drop by drop sodium thiosulphate until the color just disappears (‡) then filter; does the filtrate contain any iodine or iodides?

Mix with a little sodium nitrite, then add a few drops of starch-paste and some dilute sulphuric acid (‡). Test the delicacy of this reaction.

Add some of the iodide to a solution of ferric chloride (‡). Prove that the valence of the iron is reduced.

Add a few drops of carbon disulphide, then a little chlorine water and shake (‡); add excess of chlorine water (‡). Repeat, using bromine water (‡). Will these reactions take place in the presence of potassium cyanide?

How can chlorides, bromides and iodides be each detected in a mixture containing the three?

(For separation of these, see "Analytical Chemistry," by N. Menschutkin, Locke's Translation, p. 229.)

HYDROFLUORIC ACID.

Use a Solution of Sodium or Ammonium Fluoride.—Treat with barium chloride (‡); test the solubility of the precipitate in dilute acids (‡); does ammonia reprecipitate it?

Add calcium chloride (‡); compare its solubility with that of the barium compound (‡).

Treat with lead acetate, silver nitrate and mercurous nitrate, respectively, and compare with the other halogen acids (‡).

Mix to a thin paste, in a lead or platinum dish, finely ground calcium fluoride (fluor-spar) with concentrated sulphuric acid; cover the dish with a watch-glass or glass plate, the under side of which has been coated with melted beeswax or paraffine, through which a design has been scratched; allow to stand in a warm place for an hour or more. Remove the cover, melt and rub off the wax and note the etching of the glass. Give reactions.

Prepare a mixture as above, but containing in addition some silica or ground glass; put this mixture in a test-tube provided with a cork and outlet-tube; warm the test-tube slightly and pass the evolved gas into water (‡); filter the solution thus obtained. What does the filtrate contain? Treat a portion of it with potassium chloride (‡); to another portion add barium chloride (‡); is the precipitate soluble in dilute or concentrated hydrochloric acid? (Distinguish from sulphate.)

Mix some finely powdered borax with fluor-spar, moisten with concentrated sulphuric acid, and by means of the platinum wire insert some of the mixture into the Bunsen flame (‡).

HYPOCHLOROUS ACID.

Use a Solution of Sodium Hypochlorite.—Treat with dilute acids (hydrochloric, sulphuric, etc.) (‡); compare with chlorides. Pour a little of each of the solutions thus obtained into solutions of litmus, indigo, ferrous sulphate and potassium iodide (‡); compare with chlorine water ‡).

Treat solutions of manganous salts, lead salts and nickel salts respectively with sodium hypochlorite

(‡); if no action is observed add dilute acid (‡ . Perform similar experiments with chlorine water and compare.

Acidify the solution; add a globule of mercury and shake (‡). Repeat the experiment, using chlorine water (‡).

Add silver nitrate (‡); prove that the precipitate is silver chloride; explain the reaction.

CHLORIC ACID.

Heat potassium chlorate in an ignition-tube; what gas is given off?

Treat a very small crystal of the chlorate with concentrated sulphuric acid; note the color and odor of the escaping gas (‡); compare with chlorine. Repeat the above, using hydrochloric instead of sulphuric acid (‡). Color the hydrochloric acid with indigo and then add the chlorate (‡).

Add a solution of potassium chlorate to solutions of barium chloride, silver nitrate, lead nitrate, indigo and litmus, respectively (‡) (in the case of the last two the solutions should be acidified).

Treat the chlorate with a solution of silver nitrate and then add sulphurous acid (sulphur dioxide in water) (‡).

How could you distinguish between a chloride, a chlorate and a hypochlorite?

THE ACIDS OF SULPHUR:—HYDROSULPHURIC, SULPHURIC, SULPHUROUS, THIOSULPHURIC.

HYDROSULPHURIC ACID.

(Hydrogen Sulphide).

Use a Solution of Potassium or Sodium Sulphide.—Treat with silver nitrate (‡); test the solubility of the precipitate in nitric acid, ammonia and potassium cyanide (‡).

Add lead acetate (‡); test the solubility as above (‡) (this test may be made somewhat more delicate by the use of a solution of lead oxide in sodium hydrate instead of the lead acetate).

Treat the solution with dilute acids (‡); hold above the mouth of the tube strips of paper moistened with solutions of lead acetate, mercurous nitrate and silver nitrate respectively (‡).

Repeat the treatment with acid, passing the gas evolved into a solution of ammonia or sodium hydroxide, then add a few drops of a solution of sodium nitroprusside (‡); determine the sensitiveness of the reaction.

How would you apply these tests in the case of those sulphides which are not decomposable by acids?

SULPHURIC ACID.

Heat the sulphates of sodium, barium, iron (ferrous), aluminium and copper respectively in ignition-tubes; note differences, both in the gases evolved and in the residues obtained (‡).

Add lead acetate (:); allow the precipitate to stand (:); change on boiling (:). Repeat, using silver nitrate and mercurous nitrate respectively (:).

Add ferric chloride (:); explain. Treat with aluminium sulphate and heat (:).

Treat the solution with chlorine water, bromine water, and a solution of iodine in potassium iodide respectively (:); explain.

Treat aluminium with potassium or sodium hydroxide, then add a thiosulphate; prove that a sulphide is formed (?) (difference from sulphites).

How can you determine the presence of a sulphide, a sulphate, a sulphite, and a thiosulphate respectively, in a mixture containing all of them? Prove your method by trying it.

(See Browning & Howe, Zeit. f. Anorg. Ch., XVIII, 371, or Chemical News, LXXVIII, 213.)

dilute acids (‡)[1]; filter and add to the filtrate chlorine water or aqua regia (‡).

Treat with lead acetate, silver nitrate, and mercurous nitrate respectively (‡); in each case treat a portion of the precipitate with dilute nitric acid (‡); boil the solution containing the other portion (‡).

Reduction Reactions.—Add sodium sulphite to an acidified solution of each of the following: (1) potassium permanganate (‡); (2) potassium chromate (‡); (3) mercuric chloride (‡); (4) chlorine water (‡); (5) ferric chloride (‡), boil the latter (‡).

Oxidizing Reactions.—(1) Add hydrochloric acid to a solution of stannous chloride, then treat with sodium sulphite (‡); (2) treat zinc with dilute sulphuric acid, then add sodium sulphite (‡); pass the evolved gases into an alkaline solution of lead acetate (‡); (3) pass hydrogen sulphide into an acidulated solution (use acetic acid) of sodium sulphite and warm (‡).

THIOSULPHURIC ACID.

Heat a thiosulphate in an ignition-tube (‡); compare with sulphites (‡).

Use a Solution of Sodium Thiosulphate.—Behavior when treated with dilute acids (‡); compare with sulphites.

Add barium chloride (‡); treat the precipitate with dilute acids (‡). Repeat using calcium chloride (‡). Compare with sulphites.

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[1] Sulphite solutions are liable to contain some sulphate; the barium salt may in consequence not be entirely dissolved.

Add lead acetate (‡); allow the precipitate to stand (‡); change on boiling (‡). Repeat, using silver nitrate and mercurous nitrate respectively (‡).

Add ferric chloride (‡); explain. Treat with aluminium sulphate and heat (‡).

Treat the solution with chlorine water, bromine water, and a solution of iodine in potassium iodide respectively (‡); explain.

Treat aluminium with potassium or sodium hydroxide, then add a thiosulphate; prove that a sulphide is formed (?) (difference from sulphites).

How can you determine the presence of a sulphide, a sulphate, a sulphite, and a thiosulphate respectively, in a mixture containing all of them? Prove your method by trying it.

(See Browning & Howe, Zeit. f. Anorg. Ch., XVIII, 371, or Chemical News, LXXVIII, 213.)

solution add carefully a solution of potassium permanganate (previously acidified with sulphuric acid) until the color no longer disappears (‡). Explain.

How can you distinguish between a nitrite and a nitrate in the same solution? Try your method.

small piece of aluminium and warm (‡); hold a piece of moist red litmus paper near the mouth of the tube (‡).

Color some concentrated sulphuric acid with a drop of indigo, then add the nitrate solution (‡); now add a small amount of sodium chloride or some well-boiled hydrochloric acid, and note any difference observed (‡).

NITROUS ACID.

Use a Solution of Potassium Nitrite.—Treat with dilute sulphuric acid (‡); heat the solution (‡).

Add silver nitrate (‡); is the precipitate soluble in water? in ammonia? in acids?

To a very dilute solution of potassium iodide add a little starch-paste solution and some dilute sulphuric acid (‡),[1] then add a few drops of the nitrite solution (‡); determine the delicacy of the reaction.

Acidify a solution of ferrous sulphate with dilute sulphuric or acetic acid, then add a little of the nitrite solution (‡); warm the solution (‡). Compare with nitric acid.

Pass hydrogen sulphide into the solution (‡); acidify another portion with acetic acid, then pass in the hydrogen sulphide; note the difference (‡); heat the solution (‡).

To three or four cubic centimeters of the nitrite solution add carefully a solution of potassium permanganate (previously acidified with sulphuric acid) until the color no longer disappears (‡). Explain.

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[1] Acetic acid may also be used here, but the use of nitric or hydrochloric acids is not recommended, as these are more or less liable to contain traces of nitrous acid and of chlorine respectively, both of which would liberate iodine.

How can you distinguish between a nitrite and a nitrate in the same solution? Try your method.

another portion with sodium hydrate and test for copper in the same manner as given above for iron.

HYDROFERRICYANIC ACID.

Use a Solution of Potassium—Ferricyanide.—Treat with silver nitrate (‡). Determine the solubility of the precipitate as in the case of the ferrocyanide (‡).

To some of the solution add ferrous sulphate (‡); is the precipitate soluble in acids? In alkalies? Repeat, using ferric chloride (‡).

Treat with copper sulphate, cobalt nitrate, lead acetate and zinc sulphate respectively, and describe the reactions (‡).

Show how cyanides, ferrocyanides and ferricyanides may be detected in the presence of each other.

SULPHOCYANIC ACID.

Use a Solution of Potassium Sulphocyanate.—Treat with silver nitrate (‡); determine the solubility in ammonia, nitric acid and potassium cyanide; also its decomposition on heating (‡).

Add a few drops of ferric chloride to a dilute solution of a sulphocyanate (‡); determine the delicacy of the reaction. Is the color changed or destroyed by treatment with dilute or strong acids or alkalies? Shake some of the solution up with ether (‡); when the two liquids have separated, add drop by drop a solution of a ferrocyanide, shaking after each addition (‡).

Treat a concentrated solution of the sulphocyanate with copper sulphate (‡); try the same reaction with a dilute solution (‡).

Mix together some copper sulphate and sulphurous acid and add the mixture to a moderately dilute solution of the sulphocyanate (:); determine the delicacy of the reaction.

Treat granulated zinc with an acidified solution of the sulphocyanate (:); hold a piece of paper moistened with lead acetate over the mouth of the tube (:); explain.

THE ACIDS OF PHOSPHORUS: ORTHOPHOSPHORIC, PYROPHOSPHORIC, METAPHOSPHORIC.

ORTHOPHOSPHORIC ACID.

Heat in ignition-tubes, monosodium phosphate, disodium phosphate, microcosmic salt, ammonium magnesium phosphate and tricalcium phosphate respectively (‡). Make solutions of the residues in water or in dilute acids, set aside and test for ortho-, meta- and pyrophosphates as given below (‡).

Use a Solution of Disodium Phosphate.—Treat with calcium and barium chlorides respectively (‡); determine the solubilities of the precipitates in acetic acid and in dilute mineral acids (‡); treat the solution of the calcium salt in acetic acid with ammonium oxalate (‡), also with ferric chloride (‡). Add sodium acetate to the latter, dilute and boil (‡); filter hot, test the filtrate for calcium and phosphoric acid (‡).

Treat with magnesium sulphate (‡). Repeat, first adding ammonium chloride (why?) and ammonium hydrate; note any difference (‡); is the precipitation complete?

To a solution of sodium acetate, add two or three drops of the phosphate solution, then ferric chloride drop by drop until a red tinge appears (‡), boil the solution and filter hot (‡); save the filtrate and test for phosphoric acid by the test given below (‡); treat the precipitate with a little ammonium sulphide, shake well and let stand for ten or fifteen minutes; then filter and test this filtrate for phosphoric acid (‡); can the iron be separated from the phosphoric acid (‡).[1]

Test for the acid—acidify with dilute nitric acid; add about one and a half times its own volume of ammonium molybdate to the solution, warm to 70° C. and allow to stand (‡); solubility of the precipitate in acids and in ammonia (‡).

Add silver nitrate (‡); solubility in nitric acid and in ammonia (‡).

PYROPHOSPHORIC ACID.

Use a Solution of Sodium Pyrophosphate.—Treat with barium chloride (‡); solubility in acetic acid and in mineral acids (‡).

Add silver nitrate (‡); solubility in ammonia and in nitric acid (‡).

Add magnesium sulphate (‡); continue the addition of the magnesium salt (‡); now add ammonia (‡); boil the ammonia solution (‡) (distinction from orthophosphate).

Add ammonium molybdate (‡); to another portion first add nitric acid and boil, then add the molybdate (‡).

METAPHOSPHORIC ACID.

Use a Solution of Sodium Metaphosphate.—Add barium chloride (‡).

Treat with silver nitrate (‡); solubility (‡).

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[1] This experiment is of considerable importance, as by its means phosphoric acid may be removed from solutions in which the 2nd and 3rd Group bases are to be determined.

Add ammonium chloride, then magnesium sulphate (:) (distinction from ortho- and pyrophosphates).

Acidify a salt of each of the phosphoric acids with acetic acid and add a solution of egg-albumin; note which of the acids give a reaction (:).

How could each of the acids be detected when they are all present?

THE COMMONER ACIDS OF CARBON:—CARBONIC, ACETIC, OXALIC, TARTARIC, CITRIC.

CARBONIC ACID.

Heat several carbonates (e.g. sodium, calcium, barium and lead) in ignition-tubes (‡); repeat, using a porcelain crucible and blast-lamp (‡).

Treat a carbonate with dilute hydrochloric acid (‡); provide the apparatus with an outlet-tube and conduct the gas down into a test-tube containing calcium or barium hydrate (do not let the outlet-tube dip into the liquid); close the test-tube with the thumb and shake (‡).

Use a Solution of Sodium Carbonate.—Treat with barium chloride, calcium chloride and lead acetate respectively (‡); determine the solubility in acids (‡).

Add silver nitrate (‡); allow to stand (‡). Test the solubility in ammonia and in ammonium carbonate (‡).

How can you distinguish between a carbonate and a sulphite when both are present?

ACETIC ACID.

Heat some sodium acetate, copper acetate and lead acetate in ignition-tubes (‡); note any odor or inflammable gas given off and describe (‡).

Use a Solution of Sodium Acetate.—Add barium chloride (‡); repeat, using lead nitrate (‡).

Treat with silver nitrate (‡); if no precipitate is obtained, concentrate the solution; determine the solubility of the precipitate in water, in acids, and in ammonium hydrate (‡).

Add ferric chloride (‡); dilute largely and boil (‡). Repeat, using aluminium sulphate (‡).

Treat with concentrated sulphuric acid, cool, and add a little alcohol; warm gently and note any odor obtained (‡).

OXALIC ACID.

Heat some crystallized oxalic acid in an ignition-tube (‡), also some of each of the following oxalates: potassium, ammonium and calcium (‡).

Treat crystallized oxalic acid with concentrated sulphuric acid and heat; what gases are given off? give proof (‡).

Use a Solution of Ammonium Oxalate.—Treat with barium chloride (‡); test the solubility of the precipitate in oxalic, acetic and dilute mineral acids (‡).

Repeat the above, using calcium chloride (‡); also make similar tests, using lead and silver salts (‡).

Treat a solution of oxalic acid, or of an oxalate acidified with sulphuric acid, with potassium permanganate (‡). Explain.

TARTARIC ACID.

Heat in ignition-tubes the acid itself and several of its salts (e.g. potassium, ammonium and calcium tartrates) (‡).

Use a Solution of Potassium Sodium Tartrate (Rochelle salt).—Treat the concentrated solution with concentrated sulphuric acid and warm (‡). Explain.

Add calcium chloride (‡); test the solubility of the precipitate in the mineral acids, in acetic and tartaric acids and in sodium hydrate (‡);[1] boil the sodium hydrate solution (‡).

Test with solutions of calcium sulphate, barium chloride, copper sulphate and lead acetate respectively (‡); determine the solubilities of the precipitates in acids, in sodium hydrate and in ammonia (‡).

Add silver nitrate (‡); test the solubility in nitric acid and in ammonia (‡); boil the solutions (‡).

Repeat the above in the following manner: Take a minute quantity (about the size of a pin-head) of the solid Rochelle salt, dissolve in a little water in a *clean* test-tube and add a few drops of silver nitrate. Dilute ammonia is then added, drop by drop, till the precipitate is *nearly but not quite* dissolvèd. Dilute with water until the tube is about half full and place in a beaker of boiling water (‡ .

Use a Solution of Tartaric Acid.—Add calcium hydrate in small quantity and in excess (‡).

Treat with potassium chloride (‡); with ammonium carbonate (‡).

To separate portions of the solution, add small quantities of ferric chloride, aluminium sulphate, manganese sulphate and copper sulphate (‡); now to each add sodium hydrate (‡); what effect would the presence of tartaric acid have upon the analysis of salts of these metals?

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[1] Since sodium hydrate generally contains carbonate, the calcium tartrate precipitate will not entirely dissolve on account of the presence of calcium carbonate. It is best to filter and examine the filtrate for tartrates.

CITRIC ACID.

Treat a solution of a citrate with calcium chloride (:); boil the solution (:). Test the solubility of the precipitate in cold sodium hydrate, in ammonium chloride, and in acetic acid (:).

Treat with silver nitrate (:), dissolve in ammonia and boil (:); compare with the tartrate (:).

How can acetic, oxalic, tartaric and citric acids be detected when all are present?

BORIC AND SILICIC ACIDS.

BORIC ACID.

Use a Solution of Borax.—To the moderately concentrated solution add dilute hydrochloric acid and allow to stand; what takes place?

Treat with solutions of the following substances: barium chloride, lead acetate and silver nitrate; note whether the precipitates are soluble in: (1) excess of reagent, (2) dilute acids and (3) ammonia (‡).

Add a little hydrochloric acid, and moisten strips of tumeric paper with this solution; dry the paper and note color (‡); moisten the dried paper with sodium hydrate (‡); does hydrochloric acid restore the color?

Moisten some borax with concentrated sulphuric acid in a porcelain dish, add alcohol, warm and ignite the vapors of the alcohol (‡). How could this test be carried out in the presence of copper salts?

Mix a small quantity of borax with a little calcium fluoride, and about double the quantity of powdered acid potassium sulphate; moisten with a drop or two of water, take some of this on a platinum wire and hold in the outer Bunsen flame (‡).

Make spectroscopic tests of boric acid (‡). Compare with barium and copper.

SILICIC ACID.

Heat some finely pulverized feldspar on charcoal, also in the microcosmic salt bead (‡).

Use a Solution of Sodium Silicate.—Treat with dilute hydrochloric acid (‡); evaporate a portion of this substance to dryness in a porcelain dish; moisten with concentrated hydrochloric acid and again evaporate. What is obtained? Is it soluble in water, acids or alkalies?

Add to separate portions, ammonia, ammonium chloride and ammonium carbonate, describe what takes place in each case (‡).

Mix in a crucible some finely pulverized feldspar with 4–6 times its weight of potassium-sodium carbonate (fusion mixture), and heat at first with the lamp, until the mass fuses quietly, then for 15–20 minutes with the blast-lamp. Allow to cool; place the crucible in a beaker and extract with hot water; rinse out the crucible, acidify the solution and evaporate to dryness on the water-bath, using a porcelain or platinum dish; moisten with concentrated hydrochloric acid and again evaporate, then treat with warm water and a little dilute hydrochloric acid and filter. Examine the filtrate for bases, and prove that the residue is silica (‡).

GROUPING OF THE ACIDS.

As has been previously stated, the acids are sometimes grouped according to their behavior toward certain general reagents, such grouping being desirable in practical analytical work for purposes of elimination. Barium chloride (or, in the presence of salts of silver, lead and mercury, barium nitrate) and silver nitrate are the general reagents chiefly used.

GROUP I.—*Barium chloride* precipitates from neutral solutions the barium salt of the following acids: *chromic*, *sulphurous*, *thiosulphuric*, *iodic*, *carbonic*, *silicic*, *sulphuric*, *hydrofluosilicic*, *phosphoric*, *boric*, *hydrofluoric*, *oxalic* and *tartaric*. Of these only the sulphate and silicofluoride are insoluble in acids; carbonic, thiosulphuric and sulphurous salts are decomposed by acids, gases being evolved, while silicic is decomposed and remains as the dioxide.

GROUP II.—*Silver nitrate* precipitates from solutions acidified with nitric acid the silver salt of the following acids: *hydrochloric*, *hydrobromic*, *hydriodic*, *hydrocyanic*, *hydrosulphuric*, *sulphocyanic*, *hydroferrocyanic* and *hydroferricyanic*. These are all insoluble in acids, but are decomposed by the metallic oxides and hydroxides.

GROUP III.—*Nitric*, *nitrous* and *chloric* acids and their salts are not precipitated by either of the reagents mentioned (nitrous acid or its salts in concentrated solution is precipitated by silver nitrate, soluble on diluting).

APPENDIX.

PRELIMINARY EXAMINATION OF UNKNOWN SUBSTANCES.

Before undertaking the analysis of a compound or mixture it is always advisable to endeavor to find out as much about it as is possible, since such knowledge often determines the mode of actual procedure in carrying out the analysis, and not infrequently results in much saving of time. For this purpose certain preliminary operations or tests are resorted to, based upon the physical and chemical properties of the substance as exhibited under varying conditions. It is needless to say that for these to be of any value, they must be performed with the utmost care, note being taken of all changes and results obtained, for even apparently insignificant facts often prove of value in the light of those subsequently obtained.

A. Examination of Solutions.—One of the first tests to be made in the case of a solution is to determine its action upon litmus; according to the results thus obtained, the following conclusions may be drawn as to the constituents present:

(1) *Neutral Solutions*—may contain only water. This can be ascertained by gently evaporating a small amount to dryness in a watch-glass upon a water-

bath; if no residue is obtained, it is evident that there were no salts in solution.

A neutral solution can contain only the salts of the fixed alkalies, of ammonia, or of the alkaline earths, as the salts of the heavy metals very generally react acid when in solution.

(2) *Acid Solutions*—may contain free acids, acid salts, or the salts of the heavy metals. If the first of these only is present, upon evaporation no residue will be left, except in the case of a non-volatile acid, e.g. sulphuric, phosphoric, boric, etc.; in this latter case the residue obtained will show a very strong acid reaction.

The addition of a drop of dilute sodium carbonate solution to a few drops of the liquid to be tested, carried out in a watch-glass, will often enable one to determine to which of the above the acidity was due. If upon performing the experiment, no precipitate appears, or if one momentarily appears and then dissolves upon standing or stirring, an acid or an acid salt is probably present; if a permanent turbidity appears it is likely that the neutral salt of a heavy metal is present.[1]

(3) *Alkaline Solutions*—may contain either the hydroxides, carbonates or sulphides of the alkalies or alkaline earths, or some of the salts of the weak acids in combination with a strong basic element, e.g. the phosphates, cyanides, thiosulphates, etc., of sodium or potassium, or finally, solutions of certain of the metallic oxides in the alkalies. It is usual, after making

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[1] Too much reliance must not be put upon these conclusions, as it is evident that various causes may operate to mislead the observer.

the test just described, to determine the flame reaction, using for this purpose either the original solution, or the residue obtained from its evaporation. Great care should be taken to have the platinum wire perfectly clean before making such test, otherwise unreliable results may be obtained.

B. Examination of Solids.—The physical properties of the solids should be carefully noted. Metals or alloys often indicate their composition by their color, hardness or density; this is further proven by observing the solubility of these in various acids.

For solids other than metals, the color and other appearance of the solid should be noted, then the following tests applied:

(1) *The Flame Reaction.*—Introduce into the flame by means of a clean platinum wire a small portion of the substance. In case no color, or an uncertain color is obtained, moisten the wire in dilute hydrochloric acid and again bring into the flame—salts of volatile acids give the most satisfactory flame-tests. By this means the presence of the salts of sodium, potassium, lithium, barium, strontium, calcium, copper and boron can usually be detected.

(2) *The Bead Test.*—Many of the metallic elements, and a few of the non-metallic, exhibit characteristic behavior when heated in a bead made of borax or microcosmic salt (sodium-ammonium-hydrogen phosphate). The presence of compounds of copper, cobalt, chromium, iron, manganese and nickel can usually be detected by the color imparted to the bead when held in the oxidizing or the reducing flame of the blowpipe, or both; silicates leave an insoluble, floating skeleton

of silicon dioxide when heated in the microcosmic salt bead.

(3) *Blow-pipe Test.*—This is carried out by first heating the substance *alone* on charcoal before the blowpipe, then mixed with a flux such as dry sodium carbonate, or with a flux and a reducing agent such as potassium cyanide. The behavior of the substance under each of these conditions should be carefully noted, as thereby much information may be gained concerning its character and composition.

(*a*) On heating alone, ordinary alkaline salts fuse and sink into the charcoal; occasionally some (sodium and potassium chlorides) decrepitate, others (chlorates, nitrates) cause a rapid combustion of the charcoal.

When a residue is left after heating, if colored, it should be tested in the bead and also by fusion with a flux; if white, it should be moistened with a drop or two of cobalt nitrate and again heated sharply. This gives characteristic colored residues in the case of salts of aluminium, zinc and magnesium, also of silicates and phosphates. If the residue is white, and when treated as above gives no characteristic color, it should be tested for its alkalinity with litmus paper; the oxides of the alkaline earth metals are thus indicated.

(*b*) On heating with a flux, a metallic globule may be obtained, or an incrustation of the oxide, or both. In the event of appearances of the first, it is advisable to introduce a small amount of a reducing agent such as potassium cyanide, since some of the metallic salts are quite difficult of reduction. The following metals yield globules under these conditions:

gold, silver, copper, lead, tin, bismuth and antimony; each of these is readily recognizable by its physical properties when alone; when, however, two or more are present it is much more difficult to identify them. Arsenic, zinc and cadmium give an incrustation of the oxide without giving a bead; the former is white, accompanied by a garlic-like odor during the heating; zinc oxide is yellow when hot, becoming white on cooling, while the oxide of cadmium is yellowish brown; they can generally be identified by means of these characteristics.

(4) *Fusion on Platinum Foil.*—A small portion of the substance should be mixed with sodium carbonate and some oxidizing agent such as potassium nitrate, potassium chlorate, etc., and heated on platinum foil in the hottest part of the Bunsen flame. Colored residues indicate the presence of manganese or of chromium, which would also be shown by the bead test.

(5) *Heating in Ignition-tubes.*—On heating in a small tube closed at one end, the substance may undergo various changes which should be carefully noted.

(*a*) The substance simply melts, solidifying again on cooling; this may be accepted as an indication of the presence of salts of the alkalies or alkaline earths, of silver or mercurous chloride, or of lead chromate.

(*b*) Water is given off; it may be due to hygroscopic moisture, to water of crystallization, to the decomposition of metallic hydroxides, or to the breaking down of certain acid salts ($KHSO_4$, $MgHPO_4$, etc.). The escaping moisture should be carefully tested with litmus paper; alkalinity is generally indicative of ammonium compounds, acidity of the decomposition of acid salts, or of the salts of certain of the heavy metals which break down in the presence of water upon being heated, yielding acid vapors.

(*c*) A change of color ensues; a number of metallic oxides become yellow when hot, e.g. the oxides of zinc, tin, lead and bismuth; certain salts which contain water of crystallization change in color when this is driven off, e.g. salts of copper, cobalt, nickel, iron, etc.

(*d*) Formation of a sublimate; this may be due to salts of ammonium, arsenic or mercury, or to the vapors of sulphur or of iodine.

(*e*) Gases are evolved; significant according to the gas given off. Oxygen indicates the presence of chlorates, bromates, iodates, nitrates or of certain metallic peroxides; hydrogen indicates formates and oxalates (under certain conditions, as in presence of caustic alkalies); chlorine, bromine or iodine indicate halogen compounds, generally in the presence of oxidizing agents; sulphur indicates persulphides or thiosulphates (in the presence of salts yielding acid vapors); sulphur dioxide indicates sulphites, certain sulphates (copper), or the oxidation of free sulphur; hydrogen sulphide indicates sulphides, sulphites or thiosulphates (which sometimes yield hydrogen sulphide when decomposed in the presence of other substances); carbon dioxide indicates carbonates or oxalates (in the latter case it will be found mixed with carbon monoxide); ammonia indicates ammonium salts (especially if alkaline hydroxides, carbonates, oxides or sulphides are present); nitrogen peroxide indicates nitrates of certain of the heavy metals (lead, bismuth, etc.); cyanogen indicates the presence of sulphocyanates or of certain cyanides (silver, mercury, etc.). Each gas or vapor may be recognized by its color, odor, inflammability or other of its properties.

Certain preliminary tests are likewise sometimes employed for determining the presence of the acid radicals, but since many of these have been indicated in the preceding outline, and since it is rarely necessary that a previous knowledge should be had of what acids are present—except that it becomes necessary to know whether organic acids or phosphates are present before proceeding with the separation of the third-group metals—no outline of such preliminary tests will be given here.

In making the analysis of a given substance, the bases are always to be determined first. During this process valuable information may be obtained concerning the nature and presence of many of the acids, also as regards the character of the combinations of the acids with the bases. Further information upon these points may sometimes be obtained during the treatment of solids while effecting solution.

C. To Effect the Solution of a Solid.—Since most analytical operations are carried out in solution, it is a matter of considerable importance to select a solvent which is best suited for such purposes.

Water is naturally the best and most universally employed solvent. Next to water dilute hydrochloric acid is to be preferred. Nitric acid or *aqua regia*, though sometimes used, are not so well suited for analytical purposes, on account of their well-known oxidizing properties, which frequently produce undesired results—as in the treatment with hydrogen sulphide, in which case much free sulphur is liable to be obtained.

To bring the substance into solution the following order of procedure is recommended:

(*a*) Treat a small portion with distilled water and heat; in the event that complete solution is not obtained, filter and evaporate a few drops of the filtrate to determine if any of the substance was dissolved.

In case of partial solution, treat a portion of the substance sufficient for analysis in the manner described, washing the undissolved portion on the filter with hot water; use the water solution for analysis.

NOTE.—A portion of this solution should be used in testing for those acid radicals which are liable to be decomposed by the subsequent treatment with mineral acids.

(*b*) Treat the residue first with dilute, then, if not dissolved, with strong hydrochloric acid and warm[1] (the behavior of the substance under this treatment should be observed carefully, as frequently indications are obtained of the presence of various of the acid radicals, such as carbonates, sulphides, sulphites, cyanides, etc.).

If complete solution results, mix together small portions of the water and hydrochloric acid solutions, and, in the event that no precipitation ensues, use such a mixture for the analysis. If precipitation takes place, it is advisable to analyze the two separately.

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[1] Here, as in all such cases, it is advisable to experiment with only a small portion first, as by so doing we are frequently saved the unnecessary introduction of useless reagents which afterward have to be removed.

(*c*) In case of incomplete solution in hydrochloric acid, try nitric acid, at first alone, and then with the addition of hydrochloric acid, *aqua regia.* Under these conditions salts of silver, lead and mercury, which are insoluble in hydrochloric acid, are partially brought into solution; also certain of the metals, alloys, refractory metallic oxides and insoluble sulphides.

This solution should be evaporated to a small bulk in order to get rid of as much as possible of the free acid, then mixed with the hydrochloric acid solution and, after dilution, used for the analysis.

(*d*) That portion which remains undissolved after the above treatment must be subjected to fusion. For this purpose, it is mixed, after drying, with from four to six times its own bulk of fusion mixture[1] and a little potassium nitrate. The fusion may be effected in a platinum or porcelain crucible (in case lead, silver or the salts of other easily reducible metals are present, a porcelain crucible should always be used), by heating over the Bunsen flame until quiet fusion results, then over the blast-lamp for a considerable time, or until the decomposition is complete. The fused mass is extracted with boiling water, filtered and washed. The filtrate, after acidifying, may be tested for those acid radicals which are most likely to be present (sulphuric, silicic, hydrofluoric, chromic, arsenic, phosphoric, hydrochloric). The residue is dissolved in dilute hydrochloric or nitric acid —filtering from any insoluble portion—and tested for those metals which are most likely to be present (barium, calcium, strontium, magnesium, lead, silver, aluminium, chromium, iron, tin).

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[1] The double carbonate of potassium and sodium. This can be made by heating Rochelle salt in an open crucible until no more gas is evolved, extracting with water, evaporating the water extract to dryness and igniting the residue.

In making the analyses of such solutions as those obtained by the above described treatment, it is always well to keep in mind the fact that any great excess of reagents is to be avoided,[1] and further, that in making precipitations, the substances are precipitated in the inverse order of their solubilities, hence it is advisable to filter and test a portion of the filtrate in order to make sure of the completeness of such precipitation. The methods which are commonly employed in making a qualitative analysis are not of such a degree of accuracy that ordinary precautions may be neglected.

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[1] This can be best accomplished when the student has a knowledge of the strength of the reagents used. The author has, for his own classes, adopted the system suggested by Reddrop, Chem. News, 61, 245, 256, using the *normal* or *equivalent* basis; the strength of each solution is then indicated upon the bottle.

TABLE OF

	Potassium.	Sodium.	Ammonium.	Lithium.	Magnesium.	Barium.	Strontium.	Calcium.	Aluminium.	Chromium.	Manganese.	Zinc.	Ferrous.	Ferric.
Acetate	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Arseniate	1	1	1	1	2	2	2	2	2	2	2	2	2	2
Arsenite	1	1	1	1	2	2	2	2	....		2	.	2	2
Borate	1	1	1	1	2	2	2	2	2	2	2	2	2	2
Bromide	1	1	1	1	1	1	1	1	1	4	1	1	1	1
Carbonate	1	1	1	1m	2	2	2	2	..	..	2	2	2	.
Chlorate	1m	1	1	1	1	1	1	1	1	1	1	1	1	1
Chloride	1	1	1	1	1	1	1	1	1	4	1	1	1	1
Chromate	1	1	1	1	1	2	2	2		2	1	1	..	1
Citrate	1	1	1	1	1	2	2	2	1	1	2	2	1	1
Cyanide	1	1	1	1	1	2	1	1	...	2	2	2	4	....
Ferricyanide	1	1	1	1	1	..		1			0	2	0	1
Ferrocyanide	1	1	1	1	1	2	1	1	.		2	4	0	0
Fluoride	1	1	1	1	4	4	4	4	1	1	2	2	2	1
Hydroxide	1	1	1	1	2	1m	1m	2	2	2	2	2	1	2
Iodide	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Nitrate	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Nitrite	1	1	1	1	1	1	1	1			1	1	1	.
Oxalate	1	1	1	1	2	2	2	2	2	2	2	2	2	2
Oxide	1	1	1	1	2	1m	1m	2	4	4	2	2	2	4
Phosphate	1	1	1	1	2	2	2	2	2	2	2	2	2	2
Silicate	1	1		1	2	2	2	2	4	2	2	2	2	2
Sulphate	1	1	1	1	1	3	3	2	1	4	1	1	1	1
Sulphide	1	1	1	1	2	1	1	1			2	2	2	
Sulphite	1	1	1	1	1	2	2	2	2	2	2	2	2	1
Sulphocyanate	1	1	1	1	1	1	1	1		1	1	1	1	1
Tartrate	1m	1	1m	1	2	2	2	2	1	1	2	2	2	1
Thiosulphate	1	1	1	1	1	2	2	1	1	1	1	1	1	1

1 [illegible] in water and in [illegible] water; 1m [illegible] sparingly [illegible] in cold water [illegible] hot water [illegible] water, soluble in HCl, HNO₃ [illegible] sparingly

SOLUBILITIES

Nickel	Cobalt	Silver	Lead	Mercurous	Mercuric	Bismuth	Copper	Cadmium	Stannous	Stannic	Antimony	Arsenic	Gold	Platinum	
1	1	1m	1	1m	1	1	1	1	1	1					Acetate
2	2	2	2	2	2	2	2	2		2	2				Arsenate
2	2	2	2	2	2		2		.	....	2			..	Arsenite
2	2	2	2	....		2	2	2	2	.		.			Borate
1	1	0	1m	4	1m	2	1	1			2	1	1	1	Bromide
2	2	2	2	2	2	2	2	2						.	Carbonate
1	1	1	1	1	1	1	1	1	1	...		.			Chlorate
1	1	0	1m	4	1	2	1	1	1	1	2	1	1	1	Chloride
2	2	2	4	2	2	1	1	2	2		2		..		Chromate
1	1	2	2	2	2		1m	2					.		Citrate
4	4	0	2		1		2	2		..			1	1	Cyanide
0		0	2	2	...	0	0	2	2						Ferricyanide
0	[illegible]	0	2			2	0	2	0	0					Ferrocyanide
2	[illegible]	1	2		2	1	2	2	1	1	1	1	.		Fluoride
2	2		2			2	2	2	2						Hydroxide
1	1	0	[illegible]	2	2	2	2	1	1m	1	2	1	1	0	Iodide
1	1	1	1	1	1	1	1	1	1					1	Nitrate
1	1	1m	1	1m	1	1	1	1							Nitrite
2	2	2	2	2	2	2	2	2	2	[illegible]	2			1	Oxalate
2	2	2	2	2	2	2	2	2	2	4	2	2			Oxide
2	[illegible]	1	2	2	2	2	2	2	2	2	2	2			Phosphate
1	2		2	.			2	2							Silicate
1	1	2	4	2	1	1	1	1	1		1			1	Sulphate
2	2	2	2	2	2	1	2	2	2	2	2	2	2	2	Sulphide
2	2	2	2	2	2	1	1	1	1		1				Sulphite
1			[illegible]	2	2		2	2						2	Sulphocyanate
1	1	1	[illegible]	2	2	2	1	2	2		1				Tartrate
1		2	[illegible]	2	1		2	1							Thiosulphate

[illegible] are sparingly soluble in both water [illegible]

[illegible]

SEP [illegible] 1917

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